5-2005

Fundamental Studies of Stabilization of Polyacrylonitrile Precursor

Stephen Alan White
University of Tennessee, Knoxville

To the Graduate Council:

I am submitting herewith a thesis written by Stephen Alan White entitled "Fundamental Studies of Stabilization of Polyacrylonitrile Precursor." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Materials Science and Engineering.

Joseph E. Spruiell, Major Professor

We have read this thesis and recommend its acceptance:

G. Bhat, F. Paulauskas, R. Benson

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

To the Graduate Council:

I am submitting herewith a thesis written by Stephen Alan White entitled "Fundamental Studies of Stabilization of Polyacrylonitrile Precursor." I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Materials Science and Engineering.

Joseph E. Spruiell, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:

Vice Chancellor and
Dean of Graduate Studies

Fundamental Studies of Stabilization of Polyacrylonitrile Precursor

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Stephen Alan White
May 2005

Acknowledgments

I wish to thank all those who lent support during the completion of this work. Oak Ridge National Laboratory provided the necessary funding for this work. Dr. J.S. Lin and Dr. J.E. Spruiell gave assistance and lent their expertise in performing wide-angle x-ray scattering. Mrs. X. Ling taught the proper procedures for producing density gradient columns. Mr. V. Brantley provided training for the differential scanning calorimeter and Mr. G. Jones provided training for the scanning electron microscope. Finally Mr. D. Fielden helped assemble the heat treatment system.

I wish to thank the guidance and support of Dr. J.E. Spruiell and Dr. F. Paulauskas and would like to thank Dr. R. Benson and Dr. G. Bhat for serving on my graduate committee.

Finally, I would like to thank my family and friends for their love and support, without which, this work would not have been completed.

Abstract

The purpose of this study was to examine the stabilization of polyacrylonitrile precursor. Currently, the stabilization of polyacrylonitrile is the limiting step in the production of carbon fibers because of its cost and time requirements. By furthering the understanding of the stabilization process, it may be possible to reduce the cost and time required, allowing the widespread use of carbon fiber in several industries to be achieved.

In this study, the effects of temperature, time, environment, and pressure on the stabilization of polyacrylonitrile were examined. Once fiber samples were heat treated, four experimental techniques were used to examine the samples. The techniques were (1) wide-angle x-ray scattering, (2) density gradient column, (3) differential scanning calorimetry, and (4) scanning electron microscopy.

Temperature and time were found to play important roles in the stabilization of polyacrylonitrile. Increases in both temperature and time were found to lower crystallinity, increase the bulk density, and lower the remnant heat. The presence of oxygen in the stabilization environment was found to promote the formation of an amorphous structure, higher density, and lower remnant heat values at lower soak temperatures and soak times than would be necessary in inert environments. Both pure oxygen environment and increased pressure were found to affect stabilization, but only after 60 minutes soak time, with 0 minutes soak time giving results similar to those of air environment at atmospheric pressure, for a given temperature. Based on the results, a possible progression for the thermo-oxidative stabilization of polyacrylonitrile is

discussed, but despite the various analyses performed, it was impossible to quantify the fully stabilized state necessary for subsequent carbonization.

Table of Contents

1. Introduction 1

1.1 History of Carbon Fibers 1

1.2 Uses of Stabilized Polyacrylonitrile and Carbon Fibers 5

1.3 Objectives of the Present Research 8

2. Literature Review 10

2.1 Polyacrylonitrile Precursor 10

2.1.1 Structure of Polyacrylonitrile Homopolymer 11

2.1.2 Precursor Additions 14

2.2 Stabilization of Polyacrylonitrile 16

2.2.1 Stabilization Reactions 19

2.2.2 Morphological Changes 24

2.2.3 Shrinkage 31

2.2.4 Variations in Mechanical Properties 35

2.2.5 Thermal Behavior 38

2.3 Stabilization in Various Environments 44

3. Stabilization Versus Oxidation 48

4. Experimental Procedure 51

4.1 Materials 51

4.2 Heat Treatment of Precursor Fibers 53

4.3 Wide-Angle X-Ray Scattering 58

4.4 Density Gradient Column 60

4.5 Differential Scanning Calorimetry 60
4.6 Scanning Electron Microscopy 62
5. Results and Discussion 66
5.1 Analysis of Commercially-Treated Samples 66
5.2 Analysis of Conventionally-Treated Samples 69
5.2.1 Effect of Temperature 69
5.2.2 Effect of Time 75
5.2.3 Effect of Environment 86
5.2.4 Effect of Pressure 102
5.3 Progression of Stabilization 115
5.4 Progression of Oxidation 118
5.5 Quantifying the Stabilized State of Polyacrylonitrile 126
6. Summary and Conclusions 130
7. Future Work 134
References 135
Vita 143

List of Tables

Table 1. Broad Categories of Carbon Fibers. 3

Table 2. Properties of PAN-based Carbon Fiber. 7

Table 3. Various Comonomers for Acrylic Precursors. 15

Table 4. Properties for the Commercial and Conventional Precursors. 52

Table 5. Density Information for Commercially-Treated Samples..... 52

Table 6. Treatment Conditions for Samples Heat Treated in Nitrogen Environment..... 55

Table 7. Treatment Conditions for Samples Heat Treated in Air Environment. 55

Table 8. Treatment Conditions for Samples Heat Treated in Oxygen Environment. 56

Table 9. Samples with Densities Outside of Measurement Range. 73

List of Figures

Figure 1. Structure of Polyacrylonitrile. 4

Figure 2. General Steps in the Production of Carbon Fibers from Polyacrylonitrile. 4

Figure 3. Properties of Steel, Aluminum, and Carbon Fiber Composites..... 7

Figure 4. Morphological Model of PAN Fiber Showing Ordered and Disordered Regions. 13

Figure 5. Irregular Helix Structure of PAN Chains Suggested by Olive and Olive..... 13

Figure 6. DSC from the Stabilization Treatment of PAN Fibers. 18

Figure 7. Stabilization Reaction Schemes..... 21

Figure 8. Oxygen Profiles in Stabilized Pitch Fibers..... 25

Figure 9. Mechanism of Nitrile Cyclization in PAN and Its Copolymers..... 26

Figure 10. Infrared Spectra of PAN Fibers. 27

Figure 11. X-Ray Diffraction Patterns from Continuous Heat Treatment of Precursor Fiber..... 29

Figure 12. Proposed Structure of PAN Thermally Treated in Air..... 32

Figure 13. Effects of Heating Rate and Final Heat Treatment Temperature during Stabilization. 36

Figure 14. DSC Behavior on Heating SAF Precursor. 40

Figure 15. DSC Behavior on Heating Homopolymer PAN in Various Environments. .. 41

Figure 16. DSC Data for Three PAN Precursors and Commercially Oxidized PAN..... 43

Figure 17. Schematic Heating Profile. 54

Figure 18. Schematic of Heat Treatment System Used for Stabilization Experiments... 56

Figure 19. Wide-Angle X-Ray Scattering Pattern of PAN Precursor. 59

Figure 20. Equatorial Slice from WAXS Pattern of PAN Precursor. 59

Figure 21. DSC Scan of Conventional PAN Precursor. 61

Figure 22. Illustration for Calculation of Remnant Heat. 63

Figure 23. 50 wt% Sulfuric Acid Treatment 63

Figure 24. 25 wt% Sulfuric Acid Treatment 65

Figure 25. WAXS Scans of Commercially-Treated Samples 67

Figure 26. DSC Results of Commercially-Treated Samples. 68

Figure 27. SEM Results of Commercially-Treated Samples 68

Figure 28. SEM Micrographs of Commercial "Fully Stabilized" Fiber 70

Figure 29. WAXS Scans of Samples Treated in Air for 0 minutes Soak Time 70

Figure 30. DGC Results for Samples Treated in Air for 0 Minutes Soak Time. 72

Figure 31. DSC Results for Samples Treated in Air for 0 Minutes Soak Time 74

Figure 32. SEM Results for Samples Treated in Air for 0 Minutes Soak Time. 74

Figure 33. WAXS Scans for Samples Treated in Air at 235°C. 76

Figure 34. WAXS Scans for Samples Treated in Air at 250°C. 76

Figure 35. WAXS Scans for Samples Treated in Air at 270°C. 77

Figure 36. WAXS Scans for Samples Treated in Air at 290°C. 77

Figure 37. DGC Results for Samples Treated in Air. 79

Figure 38. DSC Results for Samples Treated in Air and Integrated up to 250°C. 79

Figure 39. DSC Results for Samples Treated in Air and Integrated up to 300°C. 80

Figure 40. DSC Scans for Conventionally-Treated Samples 80

Figure 41. SEM Results for Samples Treated in Air. 81

Figure 42. WAXS Scans for Treatment in Air at 160 and 180°C for up to 24 Hours. 82

Figure 43. WAXS Scans for Samples Treated in Air at 250°C for up to 24 Hours..... 82

Figure 44. DSC Results for Samples Treated in Air for up to 24 Hours. 84

Figure 45. SEM Results for Samples Treated in Air for up to 24 Hours..... 85

Figure 46. WAXS Scans for Treatment in Various Environments at 215 and 230°C. 87

Figure 47. DGC Results for Samples Treated at 215 and 230°C..... 87

Figure 48. DSC Results for Samples Treated at 215 and 230°C. 89

Figure 49. SEM Results for Samples Treated at 215 and 230°C..... 89

Figure 50. WAXS Scans of Samples Treated in Nitrogen. 91

Figure 51. DGC Results for Samples Treated in Nitrogen. 92

Figure 52. DSC Results for Samples Treated in Nitrogen. 92

Figure 53. DSC Scan for Conventional PAN Precursor in Nitrogen Purge Gas..... 93

Figure 54. WAXS Scans of Samples Treated in Oxygen. 94

Figure 55. DGC Results for Samples Treated in Oxygen. 95

Figure 56. DSC Results for Samples Treated in Oxygen..... 96

Figure 57. DGC Results for Samples Treated in Various Environments. 97

Figure 58. DSC Results for Samples Treated in Various Environments. 99

Figure 59. SEM Results for Samples Treated in Various Environments..... 100

Figure 60. WAXS Scans for Samples Treated at 230°C at Various Pressures..... 103

Figure 61. DGC Results for Samples Treated at 230°C at Various Pressures. 103

Figure 62. DSC Results for Samples Treated at 230°C at Various Pressures. 105

Figure 63. SEM Results for Samples Treated at 230°C at Various Pressures. 105

Figure 64. Micrographs of Samples Treated in Air at 3 Atmospheres Pressure..... 106

Figure 65. WAXS Scans for Samples Treated in Air at Various Pressures at 220°C.... 106

Figure 66. WAXS Scans for Samples Treated in Air at Various Pressures at 235°C.... 107

Figure 67. WAXS Scans for Samples Treated in Air at Various Pressures at 250°C.... 107

Figure 68. WAXS Scans for Treatment in Oxygen at Various Pressures at 220°C..... 109

Figure 69. WAXS Scans for Treatment in Oxygen at Various Pressures at 235°C..... 109

Figure 70. WAXS Scans for Treatment in Oxygen at Various Pressures at 250°C..... 110

Figure 71. DGC Results for Samples Treated at 220°C at Various Pressures. 110

Figure 72. DGC Results for Samples Treated at 235°C at Various Pressures. 111

Figure 73. DGC Results for Samples Treated at 250°C at Various Pressures. 112

Figure 74. DSC Results for Samples Treated at 220°C at Various Pressures..... 113

Figure 75. DSC Results for Samples Treated at 235°C at Various Pressures..... 113

Figure 76. DSC Results for Samples Treated at 250°C at Various Pressures..... 114

Figure 77. SEM Results for Samples Treated in Air at Various Pressures. 114

Figure 78. Concentration Distributions at Various Times..... 120

Chapter 1

Introduction

1.1 History of Carbon Fibers

Carbon fibers can be produced from either organic precursor fibers or from gas growth. Because they contain almost 100% carbon, any fibrous material with a carbon backbone could potentially be used as a precursor so long as it yields a fiber composed mainly of carbon upon heat treatment. Many naturally occurring materials such as cotton, jute, linen, ramie, and sisal, along with man-made polymers like polyester, polyamides, polyvinyl chloride, polyvinyl alcohol phenolic resins, and polyethylene have been tried as possible carbon fiber precursors, but with little success. Out of the large number of possible precursor materials, only three have received a large amount of attention due to their favorable mechanical properties upon conversion to carbon fibers. Those three are viscose rayon, pitch, and polyacrylonitrile (PAN) [1].

The first commercially produced carbon filament was made in 1879. It was made from a cellulosic precursor and used as an incandescent lamp filament. After this, cotton threads and bamboo fibers were formed into filaments of desired size and shape and heat treated until they were replicas of the original filament containing mainly carbon [1]. The first modern carbon fibers were produced from rayon fibers [2], but in time, it would be realized that PAN was a better starting material.

The thermal stability of PAN fibers was recognized soon after their development by DuPont in the 1940s. At that time, cellulose fibers and PAN homopolymer fibers

were the only fibrous substances that did not melt below their charring temperatures. Because of this, they were capable of retaining their fiber identity. Union Carbide Corporation began researching DuPont's PAN fibers as a precursor material near the end of World War II. Then, in 1950, Houtz published the first public report stating that acrylic fibers could be rendered fireproof by heat treating them in air or inert atmosphere at 200°C, prompting several companies in the U.S. to patent fireproof fabrics based on the process. The first extensive study of carbonization and graphitization of PAN fibers came in 1961 by Shindo in Japan. Shindo recognized the importance of an oxidative heat treatment step prior to the carbonization and graphitization steps, thus improving the carbon yield from PAN. He demonstrated fiber with a tensile strength of 0.75 GPa and a tensile modulus of 112 GPa, which were about three times those available from rayon-based carbon fibers of that time [1].

Since that time, PAN-based carbon fibers have come to dominate the market, with almost seventy to eighty percent of commercially available carbon fibers being derived from PAN polymer [$(CH_2CHCN)_n$] [1]. Thanks to a large amount of research, three broad categories of PAN-based carbon fibers can be produced today. These categories have been outlined in Table 1. Research into heat treatments as well as other aspects of carbon fiber production has also lead to the tensile strength of high-strength carbon fibers rising steadily from 1.4 GPa in the late 1960s to 7 GPa in the 1990s [1].

Despite the fact that there are two other important precursors from which carbon fibers can be produced, namely rayon and pitch, PAN has come to be the precursor of

Table 1. Broad Categories of Carbon Fibers.

Carbon (%)	Fiber type[a]	Heat-treatment temperature (°C)[b]	Modulus (GPa)[b]
92-96	high strength	1200-1400	228-241
99	high modulus	1800-2500	276-380
99+	ultra-high modulus	2800-3000+	483-690+

[a] In the UK, high strength fibers are called Type II and high modulus fibers are Type I
[b] Principally PAN-based carbon fibers
Adapted from [3].

choice for several important reasons: (1) its structure, which is shown in Figure 1, permits faster rate of pyrolysis without much disturbance to its basic structure and to the preferred orientation of the molecular chains along the fiber axis present in the original fiber, (2) it decomposes before melting, (3) higher degree of preferred orientation of the molecular chains is possible during spinning and drawing wherein PAN can be stretched to as high as 800%. Further improvement in the orientation is also possible during thermal stabilization when it becomes plastic at around 180°C and through various post spinning modifications, and (4) it results in high carbon yield (50-55%) when pyrolyzed to 1000°C and above [1].

A typical process for producing carbon fiber from PAN precursor is illustrated in Figure 2. Because of the unique properties that come from heat treating PAN fiber, both stabilized PAN and carbon fibers are useful in their own respects.

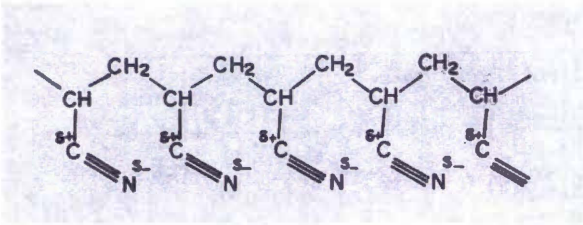

Figure 1. Structure of Polyacrylonitrile.

From [1].

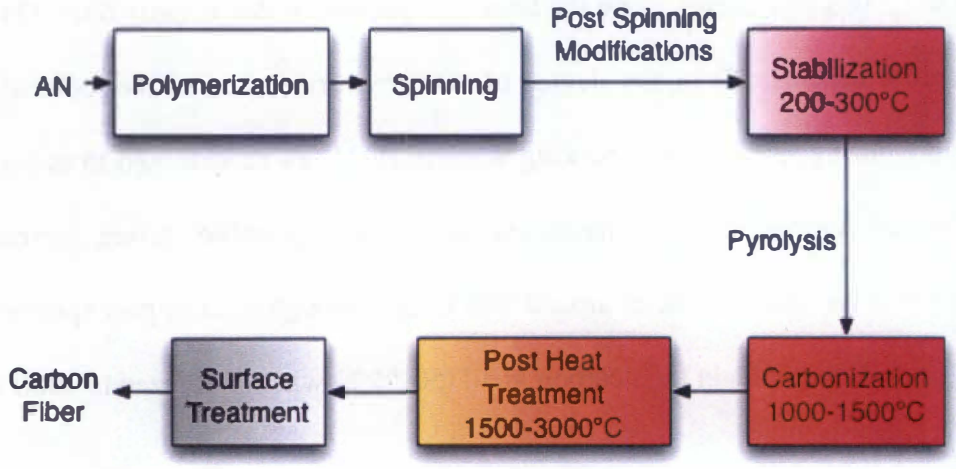

Figure 2. General Steps in the Production of Carbon Fibers from Polyacrylonitrile.

Adapted from [1].

1.2 Uses of Stabilized Polyacrylonitrile and Carbon Fibers

In the production of carbon fibers from PAN-based precursors, the precursor material must first be given a heat treatment sufficient to render the fiber infusible. This means that stabilized PAN can be used in a large number of applications that require fire resistant material. The stabilized fiber can be used in textile applications for producing yarns, woven fabrics, nonwovens, and felts.

One such use of stabilized PAN in textiles is PANOX® by SGL Carbon Group. Typical applications for PANOX ® are "fire blocking fabrics for seating in aircraft, trains, busses and cars, or protective clothing for fire fighters, armed forces and police personnel, racing drivers and steelworkers" [4]. Another such use of thermo-oxidatively stabilized PAN is PYRON® oxidized PAN fibers by Zoltek. These fibers are reported to be continuously oxidized to a carbon level of 62% and are used to replace asbestos in automotive or industrial clutches and brakes. PYRON® has also been used to make protective fabrics and chemically resistant packaging for pumps and valves [5].

On the other hand, carbon fibers lend themselves well to composite materials for several reasons: (1) carbon fibers have the higher specific modulus and specific strength than all other fiber materials used for reinforcement, (2) they retain a high tensile modulus and high strength at elevated temperature, though high temperature oxidation may prove problematic, (3) carbon fibers are not affected by moisture or a wide variety of solvents, acids, and bases at room temperature, (4) they exhibit a large range of physical and mechanical characteristics, allowing their composites to have specifically

engineering properties, and (5) relatively inexpensive and cost effective manufacturing processes for fiber and composite materials have been developed [6].

Table 2 details some properties of PAN-based carbon fibers, while Figure 3 compares various properties of steel, aluminum, and carbon fiber composites. Carbon fibers can be used in several processes to make composite materials, such as sheet molding, filament winding, and pultrusion processes [7]. Because of their favorable strength to weight ratio, carbon fiber composites have become extremely important in the design of both civilian and military aircraft, often replacing aluminum in all but the main structural components [2, 8]. Carbon fibers are also becoming the material of choice in a number of other applications. Medical applications of carbon fibers include Thermocomp RC, a carbon fiber reinforced nylon 6/6 composite that is being used in the exoskeletal structure of a prosthetic arm [9] and the Omnicarbon heart valve, which is the only monoleaflet valve (a valve with a single hingeless pivoting disk) to make use of pyrolytic carbon in both its housing and disk for improved biocompatibility [10]. Other monoleaflet valves have metal or non-pyrolytic-carbon-coated metal housings [10]. The sporting goods industry also uses carbon fiber composites, using them to make inline skates [11], golf clubs, and tennis rackets.

Recently, carbon fibers have been incorporated into automobiles as well. One such application is the body of the car, where carbon fiber composites can be used to reduce weight while providing the same strength as traditional materials. Carbon fiber/epoxy composite body parts are being developed for the Lamborghini Murcielago

Table 2. Properties of PAN-based Carbon Fiber.

Property	High strength[a]	High modulus[b]	Ultra-high modulus[c]
Filament diameter (μm)	5.5-8.0	5.4-7.0	8.4
Density (g/cc)	1.75-1.80	1.78-1.81	1.96
Carbon content (wt %)	92-95	99-99+	99+
Tensile strength (MPa)	3105-4555	2415-2555	1865
Tensile modulus (GPa)	228-262	359-393	517
Elongation at break (%)	1.3-1.8	0.6-0.7	0.38
Electrical resistivity ($\mu\Omega$•m)	15-18	9-10	6.5
Thermal conductivity (W/m/K)	8.1-9.3	64-70	ca 120

[a] Thornel T-300, T-500, T-600, T-700, Union Carbide Corp.; Celion 3000, 6000, 12000, Celanese Corp.; AS2/AS4/AS6/IM6, Hercules Corp.

[b] Thornel T-50, Celion G-50, HMS, Hercules Corp.

[c] Celion GY-70

All data is based on strand data. Adapted from [3].

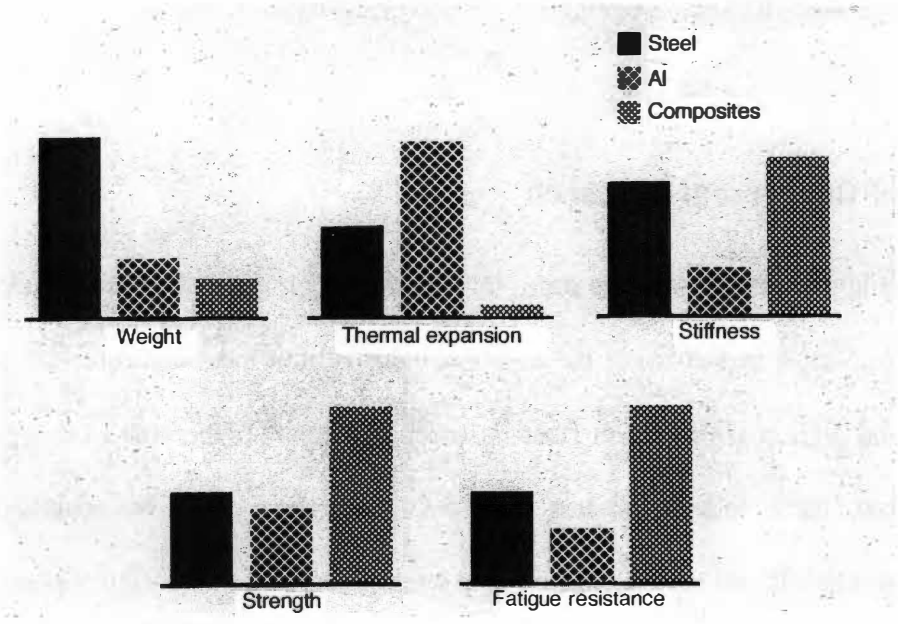

Figure 3. Properties of Steel, Aluminum, and Carbon Fiber Composites.

From [3].

[12] as well as the hood of the 2004 Chevrolet Corvette Z06 [13]. The space frame of the car can also use carbon fibers to help lower weight while maintaining strength. Foam cores covered with braided carbon fiber sleeves have been designed for building up vehicle structures such as space frames, truck chassis assemblies, or vehicle trailers [14]. The structures should offer stiffness similar to automotive steels, with higher failure strength and less than 40% of the weight of steel. The material also has the benefit of failing in a progressive and controlled manner during collision [14]. Other applications include carbon fiber-reinforced fluoropolymers designed to replace pump wear rings, throat bushings, line shaft bearings, valve seats and washers [12]. These parts must operate in hostile chemical environments, providing superior creep resistance at high temperature, inherent strength, stiffness, and dimensional stability.

1.3 Objectives of the Present Research

All of these applications have one thing in common: high cost. The automotive industry has shown interest in following the aviation industry, but has been reluctant to do so because of the high cost of carbon fiber-based composites. If the cost of carbon fibers were lowered, their widespread use in several industries could be achieved. Specifically, the automobile industry would be able to produce cars that weigh less and are more fuel efficient while still being as safe to drive as the cars currently produced today. Other research has looked into the possibility of using carbon fibers and other

carbon products to store hydrogen for use in fuel cell-powered automobiles [15, 16, 17, 18, 19, 20].

Currently, the stabilization of PAN precursor is the limiting step in the production of carbon fibers. The stabilization step is both costly and time consuming. By furthering the understanding of stabilization, it may be possible to reduce both the time and cost required. The objectives of this work are to study the effects of not only temperature and time on stabilization, but also the effects of varying the environment in which stabilization is conducted and the atmospheric pressure under which stabilization is conducted.

Chapter 2

Literature Review

2.1 Polyacrylonitrile Precursor

The production of carbon fibers from PAN-based precursor generally involves three steps. First, the precursor fiber must undergo stabilization with low heating rates and carefully controlled temperatures in order to convert the precursor into an infusible form that can be further heat treated. This step is usually carried out in oxygen-containing atmosphere such as air, due to the beneficial effects that air has on the stabilization of PAN. The second step is a carbonization treatment carried out in an inert atmosphere. This treatment is used mainly to eliminate the majority of non-carbon atoms from the structure. The third and final step is graphitization, which is carried out in an inert atmosphere at high temperatures. This heat treatment stage eliminates the remaining non-carbon atoms and develops the final carbon morphology. This process is depicted graphically in Figure 2.

Of the three steps stated, the stabilization stage is the most costly and time consuming. A heat treatment program controlling both heating rate and maximum heat treatment temperature must be used to control the large exothermic reactions that PAN undergoes as it is heat treated. Proper heat treatment results in retention of high temperature properties as well as an increased yield in solid material. If the exothermic reactions are allowed to become destructive, however, generation of volatile gases, liquids, and waxes can occur. Also, excessive weight loss will occur accompanied by

chain scission, fusion, or even burning of the fibers. The stabilization step has been the subject of numerous studies because of its cost and the number of chemical reactions that take place, but despite the large amount of research, the stabilization step is not fully understood.

2.1.1 Structure of Polyacrylonitrile Homopolymer

The structure of PAN has been studied extensively in the literature, but the exact details behind its morphology are still mostly unknown. When the bulk polymer is oriented, intense equatorial reflections are observed during wide-angle x-ray diffraction (WAXD) experiments. These reflections correspond to spacings of approximately 3.0 and 5.3 Å measured normal to the chain direction. While these reflections are intense, off equatorial reflections are diffuse, leading some researchers to conclude that a definite repeat distance along the polymer chain does not exist. The morphology has been considered by some as that of a single-phase laterally ordered polymer; it has been given a planar unit cell and called a two-dimensional crystal by others. Some researchers describe the morphology as a paracrystalline, liquid crystal texture while others have concluded that three-dimensional crystallinity does exist in PAN and have defined an orthorhombic unit cell or a hexagonal unit cell [21]. Information from both wide angle x-ray diffraction and electron microscopy studies show clearly the presence of a basic morphological unit with a lateral dimension of the order of 5 to 10 nm in which the molecules are arranged in a laterally ordered hexagonal array [22].

Dalton et al. [23] performed heat treatments on Special Acrylic Fiber (SAF) precursor and homopolymer PAN fiber, DT. Using a synchrotron source, seven equatorial wide-angle x-ray scattering (WAXS) reflections could be detected in the homopolymer PAN fiber bundles. Sharp meridional peaks could also be observed under certain conditions. They state that PAN may best be perceived in terms of lateral ordering of distorted rod-like molecules, with small regions of three-dimensional crystallinity.

Warner et al. [21] have proposed a new model for the morphology of PAN based on their findings, as shown in Figure 4. They propose that the structure of acrylic fibers consists of elongated voids and fibrils. The fibrils are composed of bundles of rods 50 to 100 Å along the length of the fiber with 30 to 70 Å amorphous regions. Within the ordered domains, the nitrile groups are oriented at a variety of angles to the fiber axis, are interpenetrating between adjacent rods, but tend to repel one another along a given rod. The research of Jain and Abhiraman [22], Jain et al. [24], and Pinghua et al. [25] supports this morphological model.

The large dipole moment of the nitrile groups, together with their close proximity in space, leads to very large intramolecular dipolar and steric repulsions that compel the individual macromolecules into a somewhat helical conformation. As shown in Figure 5, the twisted, kinked molecule may be thought of as a more or less rigid structure, fitting within a cylinder, which is not appreciably deformed on drawing. The random orientation of nitrile groups in space in this model explains the observed low infrared dichroic ratios and optical birefringence [26].

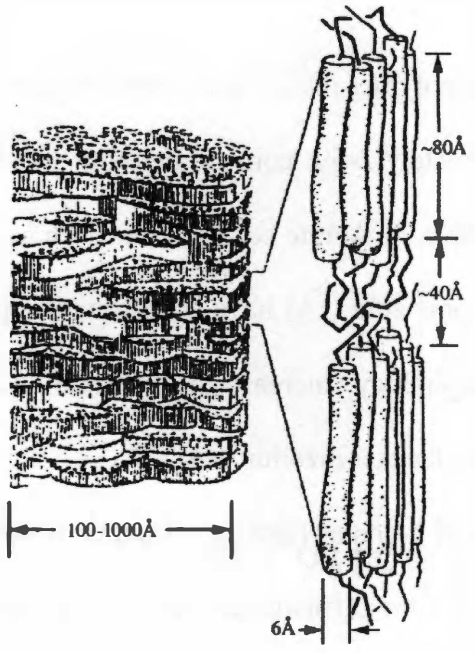

Figure 4. Morphological Model of PAN Fiber Showing Ordered and Disordered Regions.

From [21].

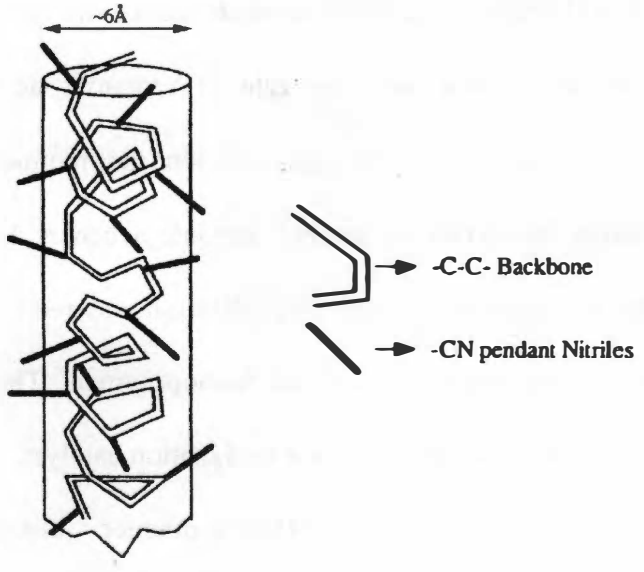

Figure 5. Irregular Helix Structure of PAN Chains Suggested by Olive and Olive.

From [26].

2.1.2 Precursor Additions

It has been found that using PAN homopolymer results in a poorer quality carbon fiber than does copolymer PAN with approximately 2-5% comonomer additions [1]. A list of various comonomers can be found in Table 3. Acidic comonomers such as acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA) have been found to provide supplemental dye sites, modify the fiber morphology, increase the hydrophilicity, and facilitate the cyclization of nitrile groups during the stabilization step [27].

It has been found that the stabilization of 3-denier fibers that contain a weak acid comonomer, such as itaconic acid, are limited by the diffusive transport of oxygen when heat treated in air at temperatures between 220 and 230°C. When similar fibers not containing a weak acid comonomer were heat treated under similar conditions, it was found that stabilization was limited by reaction rate [28].

In their studies, Bajaj et al. [27] found that acid comonomers reduce the initiation temperature of cyclization/dehydrogenation reactions, the rate of reaction, and the activation energy, finding that itaconic acid seemed to be more efficient that methacrylic acid. Fitzer and Müller [29] studied the effect of methyl acrylate when added to precursor material. They found that the activation energy of cyclization was reduced in the case of copolymer with methyl acrylate compared with the homopolymer. This led them to conclude that the comonomer methyl acrylate acts as a cyclyzation catalyst.

Other researchers have gone about treatment in a different manner. Instead of studying the effects of comonomer additions, Mathur et al. [30] treated as-received

Table 3. Various Comonomers for Acrylic Precursors.

Comonomers	Chemical structure
Acrylic acid	CH_2=CHCOOH
Methacrylic acid	CH_2=C(CH_3)COOH
Methacrylate	CH_2=CHCOOCH_3
Acrylamide	CH_2=CHCOONH_2
Itaconic acid	CH_2=C(COOH)CH_2COOH

Adapted from [1].

Courtelle fiber tows with potassium pernamganate solution at temperatures of 85, 90, and 95°C for times varying from 3 to 30 minutes. If was found that a temperature of 85°C resulted in the best treatment due to the severe reaction between PAN and potassium permanganate solution at high temperatures. It was found that the activation energy for cyclization decreased from 119 kJ/mol for unmodified precursor to 90 kJ/mol for samples treated in solution for 20 minutes. It was also observed that the total heat flow initially increased slightly for a treatment time of 3 minutes, but then decreased for samples treated for 20 and 30 minutes. The initiation temperature for cyclization was lowered for samples treated for 10 and 20 minutes, but the peak of the exotherm remained the same, indicating that the exotherm for modified samples is spread over a broader temperature range as compared to untreated samples.

Mascia and Paxton [31] pretreated precursor fibers with gamma radiation at a dose rate of 25 kGy/hour to a total dose of 150 kGy prior to constrained heat treatment in a forced air-circulation oven at 250°C. It was found that pretreatment with gamma radiation can accelerate the oxidation process appreciably. Greater molecular

fragmentation took place during oxidation when the fibers were pretreated with radiation, but the overall weight loss was reduced.

Bhanu et al. [32] studied copolymers with various amounts of methyl acrylate (MA) polymerized utilizing several methods. It was found that copolymers containing about 15 mol% MA are potential carbon fiber precursors.

Wangxi et al. [33] compared the stabilization of precursor material containing itaconic acid with precursor material containing acrylamide. It was found that acrylamide appears to be more effective at separating the exothermic reactions as compared to itaconic acid. Also, except for the ideal chemical composition, the optimal PAN precursor should have higher density, higher and adequate strength, higher crystallinity, and a preferred morphology with as few voids as possible. Wangxi et al. state that the need for high strength PAN precursor is not necessarily essential in order to obtain high performance carbon fibers because of the important role that chemical composition and fiber morphology play during stabilization and carbonization.

2.2 Stabilization of Polyacrylonitrile

A stabilized fiber is considered suitably stabilized when its oxygen content is in the range of 8 to 12%. It has been found that an oxygen content lower than 8% results in a low yield of carbon fibers due to excessive weight loss during the carbonization heat treatment. An oxygen content of more than 12% has been found to result in the deterioration of stabilized fiber quality, which results in low quality carbon fiber [26]. It

has been theorized that oxygen is essential for the completion of stabilizaton reactions. It promotes the formation of double bonds and cross links in the stabilized structure via hydrogen stripping reactions, forming a structure that is less susceptible to cleavage during the carbonization step [34].

Just as there is debate in the literature as to the structure of PAN, there is also debate as to the proper course to take for stabilization of PAN precursor. Fitzer et al. [35] state that, based on DSC measurements, the stabilization reaction has to be stopped at 270°C to avoid over-oxidation of the fiber. For their precursor, 270°C lies just after the first peak in the differential scanning calorimetry (DSC) curve, as shown in Figure 6. Gupta and Harrison [36], however, state that a final heat treatment temperature of ~380°C seems to be necessary for complete oxidative stabilization, in agreement with Mathur et al. [37], who found that stabilization is not at all complete at temperatures below 300°C. Mathur et al. state that a minimum temperature of 350°C and a maximum temperature of 400°C seems to be essential for proper stabilization. It was found that samples stabilized at higher temperature had lower hydrogen contents. This was suggested to provide a highly thermally stable aromatic structure for further heat treatment at higher heating rates and to decrease the production of tar, thus increasing yield and providing a better carbon fiber structure.

Fitzer et al. [35] did show that a heating rate of 1 to 3°C/min during stabilization seemed to be ideal for producing carbon fibers with the maximum tensile strength. Of the temperatures and heating rates under consideration in their study, a heating rate of 1°C/min up to 270°C produced a carbon fiber with the highest tensile strength.

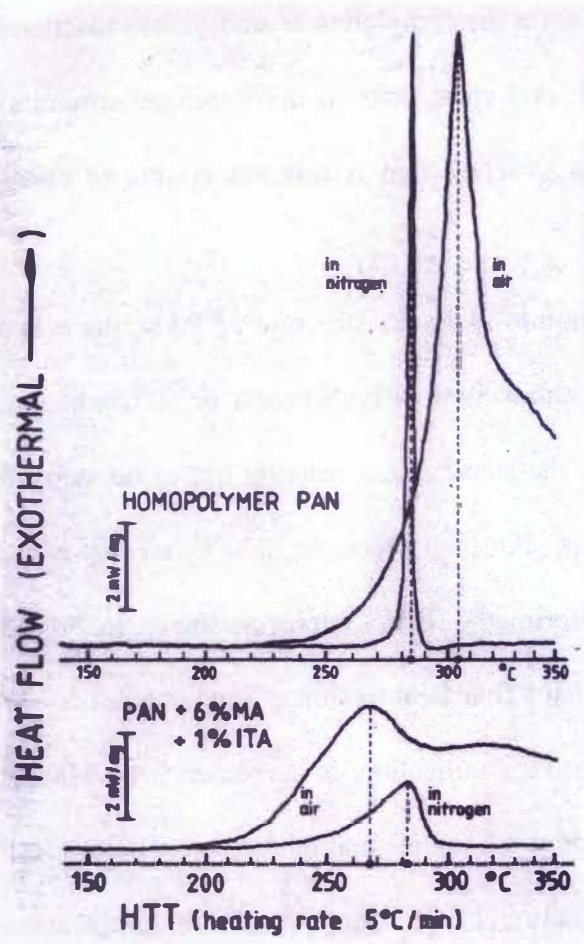

Figure 6. DSC from the Stabilization Treatment of PAN Fibers.

PAN fibers of varying compositions were tested in both nitrogen and air environments. The composition and environment are indicated [8].

Although controversy still exists, the following statements can be made: (1) the presence of oxygen in the stabilizing atmosphere promotes the initiation of cyclization, and this initiation is involved with chain scission and the formation of initiator sites; (2) as the temperature is raised, chain scission, the number of initiator sites, and the overall kinetics of the stabilization process are increased; (3) oxygen participates in a number of cross-linking reactions, i.e., at the chain end, after scission, and on the polymer backbone; (4) dehydrogenation reactions, promoted by an oxidative environment, lead to a conjugated and planar backbone structure, which combined with cyclization, yields a pre-structure of sheet-like character capable of being stacked, a preferred arrangement for subsequent carbonization; and (5) the combined effects of chain scission and the tacticity of PAN (random atactic) preclude long segments of cyclized chains from being formed [3].

2.2.1 Stabilization Reactions

During the stabilization of PAN precursor, several reactions take place. These reactions are not well understood, but have been generalized as cyclization, which involved the polymerization of the nitrile groups, dehydrogenation, and oxidation. During stabilization in oxygen-containing atmospheres, dehydrogenation and oxidation take place naturally, but these reactions do not take place in inert atmospheres. Using electronic and IR spectra collected from samples stabilized from 140 to 200°C, temperatures not usually associated with the stabilization of PAN, Platonova et al. [38]

showed that the formation of polyene sections first precedes cyclization and then the two processes occur in parallel. Also, Fitzer and Müller [29] showed that cyclization and dehydrogenation reactions occur simultaneously based on DSC data taken in an air atmosphere. All of these results, however, are based on much earlier work on the stabilization of PAN precursor.

In 1950, Houtz noticed that the heat treatment of PAN led to coloration, but not to rapid depolymerization at elevated temperature as in other vinyl polymers. He proposed a conjugated, fully hetero-aromatic cyclic structure to account for the changes taking place during heat treatment, such as coloration, insolubility, and flame resistance. The cyclization concept has since been modified by many subsequent researchers. Grassie et al., Burlant and Parsons, and LaCombe changed Houtz's cyclization scheme to a partially aromatic structure. This has since become the most popular reaction scheme quoted in the literature. The partially aromatic structure is also called a ladder polymer [39]. A number of reaction schemes are listed in a roughly chronological order in Figure 7.

Ogawa and Saito [40] recorded IR spectra of fibers heat treated for various times at 242°C in air. It was found that as the fibers were more fully oxidized, the absorption band at 2240 cm^{-1}, assigned to the nitrile group, decreased. Also, absorption bands at 1750 to 1600 cm^{-1}, assigned to C=O and NH—C=O groups, 1590 to 1570 cm^{-1}, assigned to C=N and C=C groups, and 1400 to 1000 cm^{-1}, assigned to C—N and C—O—C groups increases with increasing stabilization.

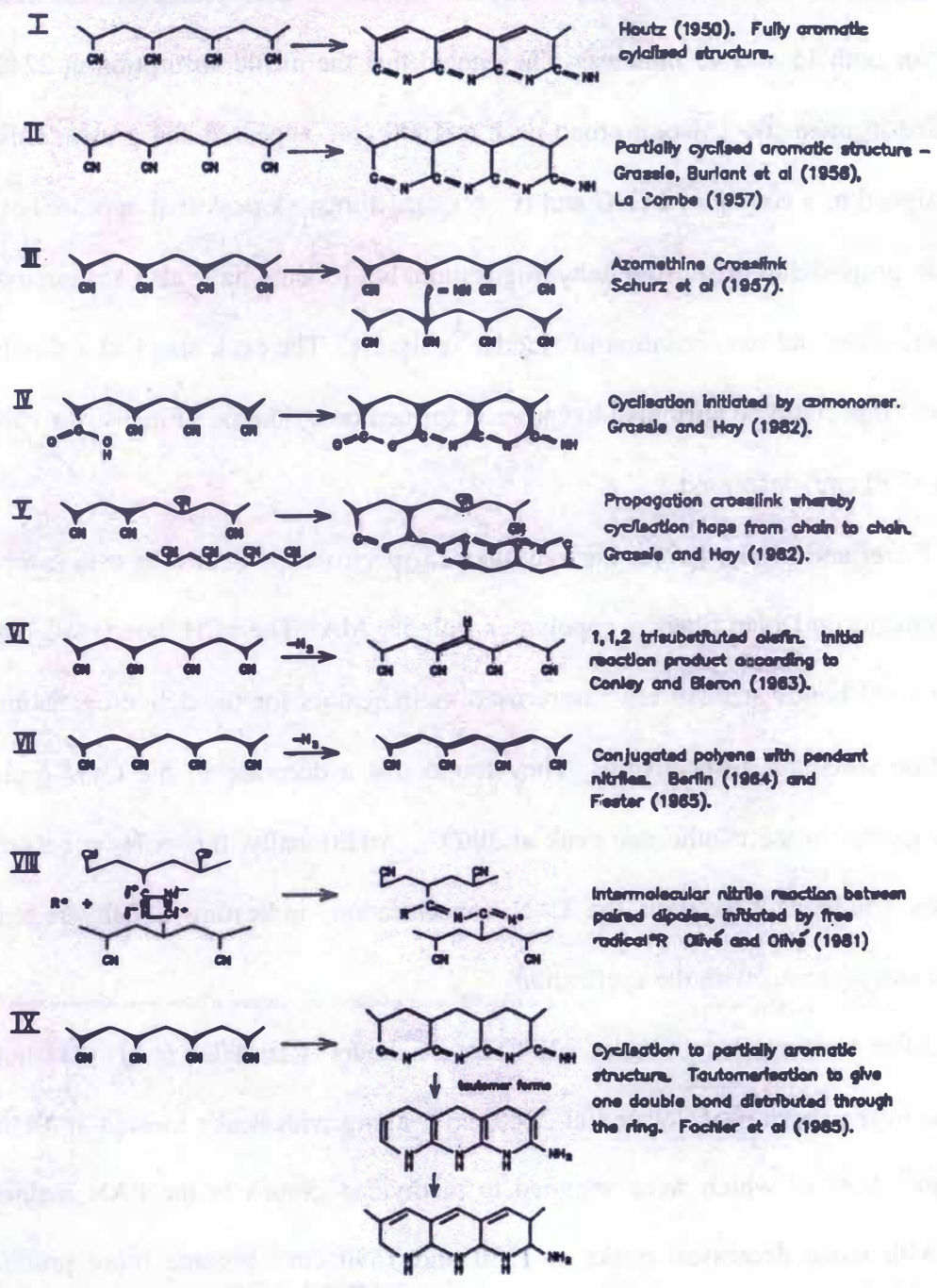

Figure 7. Stabilization Reaction Schemes.

From [39].

Dalton et al. [23] recorded polarized IR spectra of SAF precursor heat treated at 225°C for both 15 and 45 minutes. They noted that the nitrile absorption at 2240 cm^{-1} decreased in intensity. Also, a broad peak at 1600 cm^{-1} appeared and grew. This peak was assigned to a conjugated C=C and $(C=N)_n$ structures. A peak that appeared at 2200 cm^{-1} was proposed to arise from dehydrogenation, but it could have also appeared due to tautomerization and isomerisation of "ladder" polymer. The peak also had a shoulder at 1680 cm^{-1} that could be attributed to carbonyl formed on oxidation. Finally, the carbonyl peak at 1730 cm^{-1} decreased.

Fitzer and Müller [29] compared infrared spectroscopy data with data from DTA measurements on Dolan fibers, a copolymer with 5% MA. The $=CH_2$ bonds at 2940 cm^{-1} and the C≡N bonds at 2240 cm^{-1} were used as indicators for the dehydrogenation and cyclization reactions, respectively. They found that a decrease of the C≡N groups is directly related to the exothermic peak at 300°C. Additionally, the $=CH_2$ concentration decreases simultaneously with the C≡N concentration, indicating a dehydrogenation reaction simultaneous with the cyclization.

After treating PAN film at 220°C for 16 hours, Renschler et al. [41] noted a decrease in the sharp peak located at 2240 cm^{-1}, along with peaks located at 1430 and 2940 cm^{-1}, both of which were assigned to methylene groups in the PAN mainchain. Along with those decreases, peaks at 1380 and 1590 cm^{-1} became more prominent. These peaks were assigned to carbon-carbon and carbon-nitrogen double bonds.

Ubbrìaco et al. [42] had the opportunity to record FTIR spectra from a commercially stabilized PAN precursor. It was found that the oxidized PAN fiber was

mainly opaque to infrared rays. A very weak band was noted at 2241 cm^{-1}, indicating a residue of the nitrile groups in the pre-oxidized fiber.

Love et al. [43] examined heat-treated PAN fibers using electron probe microanalysis. The precursor used was 1.8 denier Orlon PAN precursor, a bean shaped fiber containing 6% methyl acrylate. The first batch was treated in air for 1 hour at 240°C. The second batch was treated in vacuum for 1 hour at 230°C and then treated in air at 230°C for 1 hour. 1 μm sections were mounted onto carbon film supported on copper microscope grids. These were then coated with 100 Å of gold. While the specimens treated in air showed no visible oxygen gradient across the cross section, the specimens treated in vacuum and air showed a two-zone morphology and an oxygen gradient was detected across the cross section. It was determined that the rate controlling process for samples treated in air was the oxidation reaction. It is stated that the rate of reaction is determined by the rate at which ladder polymer is formed. Since this is a slow process relative to the oxidation reaction, oxygen can diffuse through the specimen sufficiently fast to oxidize all the ladder polymer as it forms. In samples treated in vacuum then air, the process is changed to oxygen diffusion. Since the ladder polymer oxidizes more readily than the initial polymer due to the formation of activated methylene groups, a high rate constant occurs, ensuring that the reaction is diffusion limited and that zoning occurs.

Blanco et al. [44] performed electron probe microanalysis on pitch fibers with a diameter of 100 μm. The fibers were stabilized in a vertical furnace pre-heated to temperatures of 160, 180, and 200°C for times varying from 2.5 to 100 hours. The

samples were then mounted vertically in resin and polished in a conventional manner. An oxygen gradient was found along the fiber cross-section and can be seen graphically in Figure 8.

Proposed reactions for nitrile cyclization can be seen in Figure 9. Figure 10 shows IR spectra of two PAN precursors heat treated in a forced-air-circulating oven for one hour at 250°C.

2.2.2 Morphological Changes

Burlant and Parsons [45] studied the degradation of polyacrylonitrile heat treated in both nitrogen and air environments. Below 200°C, the material remained essentially unchanged. As the temperature was raised, the material changed color from yellow to red to brown to a blue-black color. As the material changed color, it was found that the material became insoluble in dimethyl formamide, a common solvent for PAN. The researchers also noted that the characteristic Bragg reflection at 5.3 Å in PAN disappears in the heated sample.

Jain and Abhiraman [22] heat treated fibers under constant length conditions at 270°C for up to 128 minutes and gathered flat plate WAXD data. The data show that the crystalline peak in the precursor material slowly decreases in intensity with increasing heat treatment time and finally is replaced after 128 minutes with a large amorphous region. Warner et al. [21] state that WAXD data show a continuous decrease in the amount of ordered domains upon heat treatment.

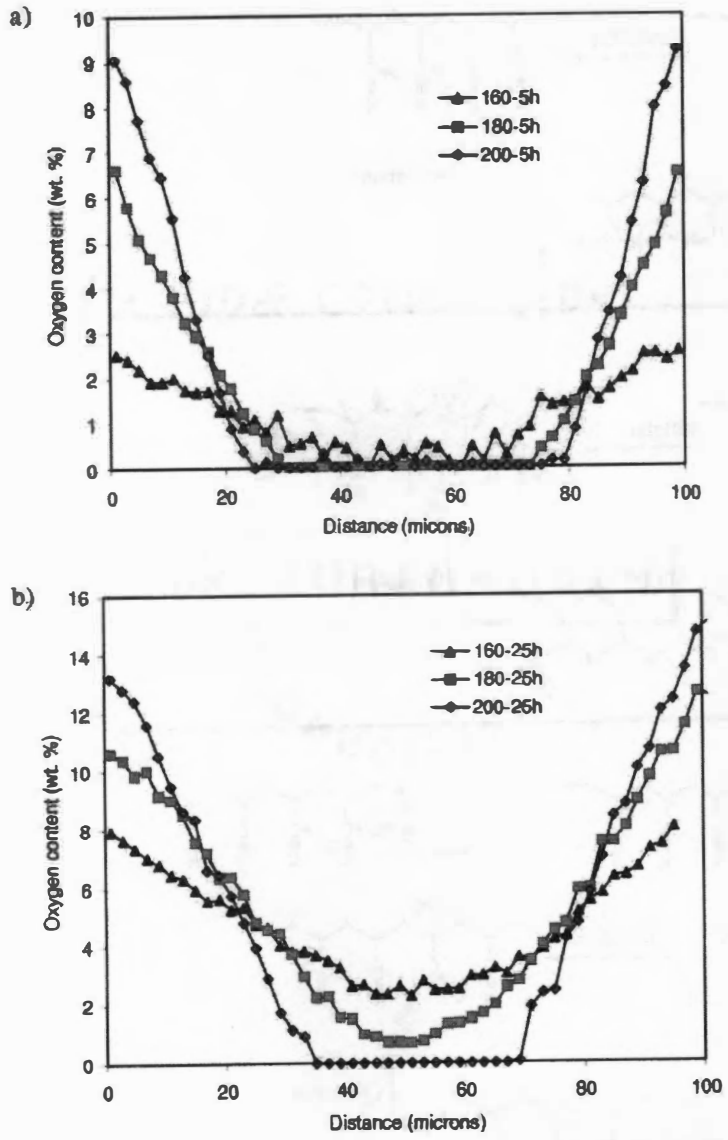

Figure 8. Oxygen Profiles in Stabilized Pitch Fibers.

The fibers were stabilized at the indicated temperatures for (a) 5 hours and (b) 25 hours [44].

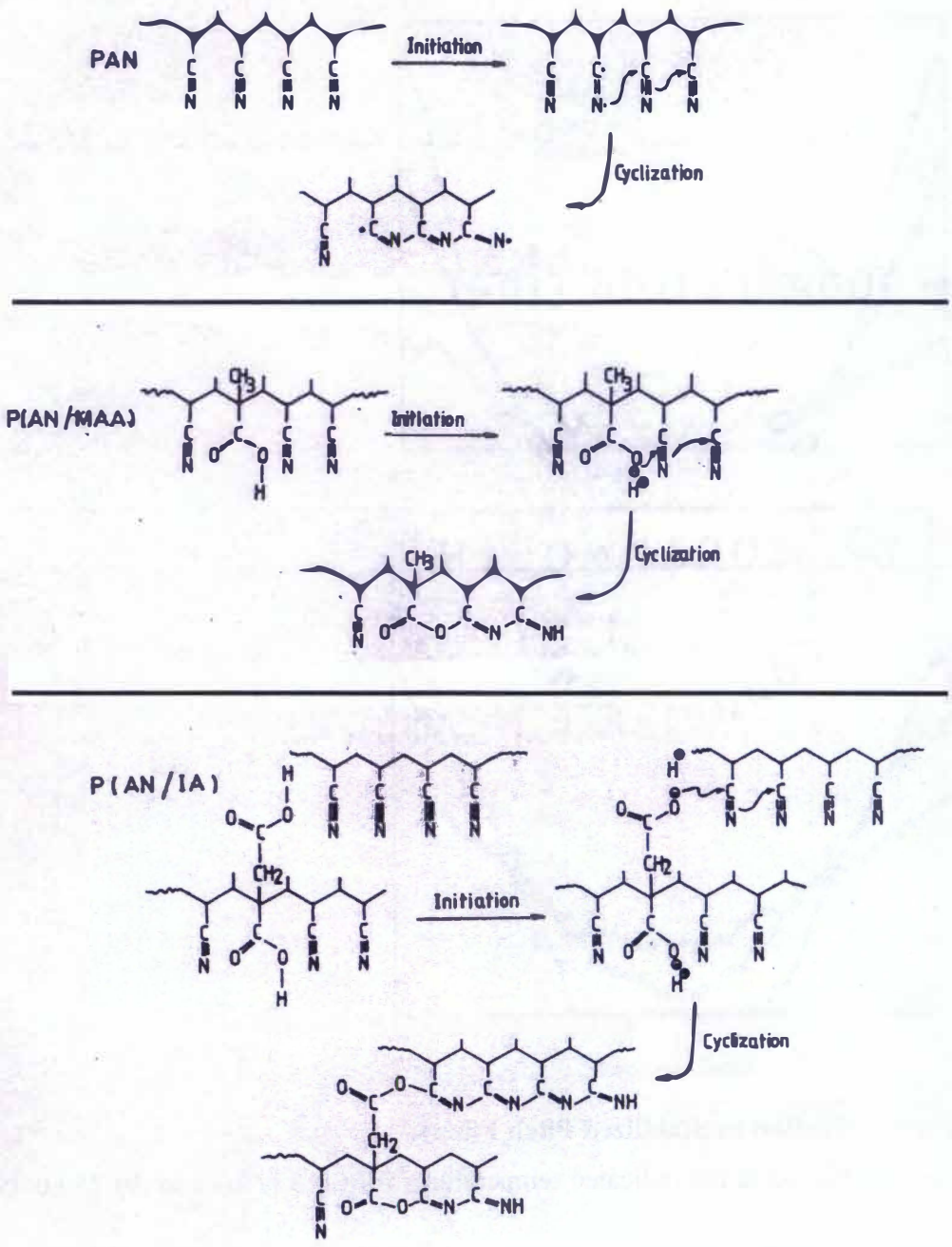

Figure 9. Mechanism of Nitrile Cyclization in PAN and Its Copolymers.
From [27].

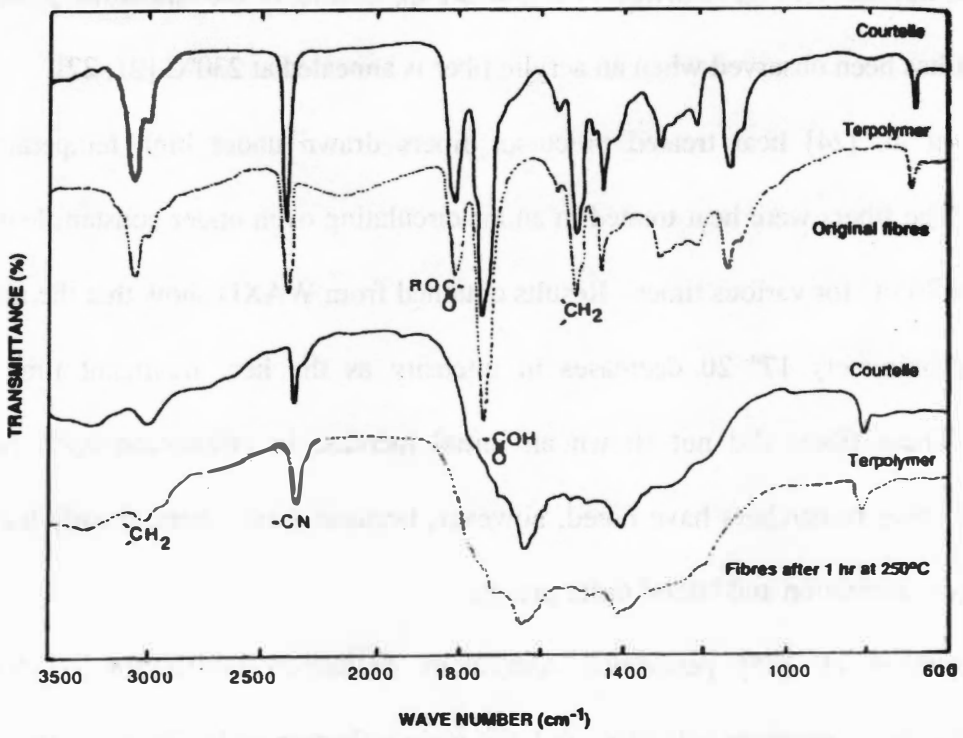

Figure 10. Infrared Spectra of PAN Fibers.
From [31].

An initial sharpening, followed by a gradual broadening of the equatorial peak in WAXD data has been observed when an acrylic fiber is annealed at 230°C [21, 22].

Jain et al. [24] heat treated precursor fibers drawn under high temperature conditions. The fibers were heat treated in an air-circulating oven under constant length conditions at 265°C for various times. Results obtained from WAXD show that the main peak at approximately 17° 2θ decreases in intensity as the heat treatment time is increased. These fibers did not shown an initial increase in orientation upon heat treatment as other researchers have noted, however, because these fibers already had a high degree of orientation and lateral order present.

Pinghua et al. [25] performed continuous oxidative stabilization on SAF precursor. As the temperature was increased, the main reflection at 17° 2θ diminished in intensity and increased in width, indicating a decrease in ordered domains, as shown in Figure 11. At about 245°C, a new diffuse scattering at 25.5° 2θ developed, which sharpened considerably and approached the (002) spacing in the consequent carbon fibers during the carbonization treatment. This suggests the formation of new morphological structure attributed to development and stacking of aromatized ladder structure in the oxidized fibers.

By combining WAXD and sonic modulus measurements, Pinghua et al. [25] found that the progression of morphological structure of acrylic fiber, when treated under drawing conditions, goes through three steps during the continuous stabilization stage. An apparent initial increase in orientation and extent of order is observed, then the

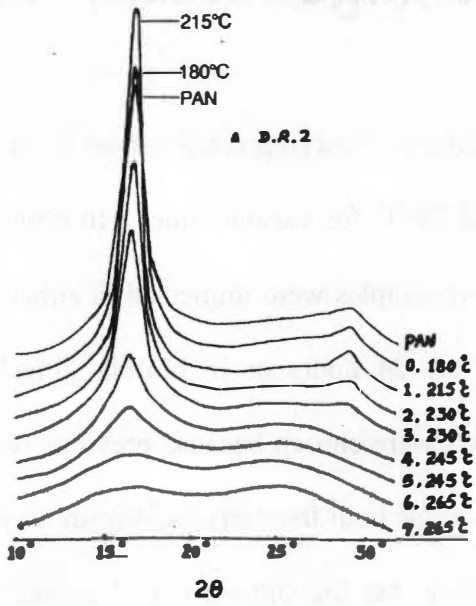

Figure 11. X-Ray Diffraction Patterns from Continuous Heat Treatment of Precursor Fiber.

From [25].

morphological order shows a rapid decrease with the occurrence of significant chemical reactions. This is followed by a slow change in measurements. A new morphological structure was found to develop in the later stages of stabilization. This new structure was attributed to the formation and stacking of aromatized ladder structure.

Jain and Abhiraman [22] have conducted experiments showing that significant morphological rearrangements take place in acrylic precursor fibers at temperatures comparable to those in a stabilization process. By annealing fibers for 2 minutes at 230°C, it was shown that a significant increase in orientation occurs when a constraint against shrinkage is imposed. When a constraint against shrinkage is not imposed, a considerable decrease in overall fiber orientation occurs, but the ordered phase increases

in orientation. This indicated that the precursor fiber is composed of a second phase that makes up a large portion of the material.

Warner et al. [28] heat treated precursor fibers of varying composition in an air circulating oven at temperatures between 220 and 230°C for various times. In order to examine the effects of the heat treatments, the fiber samples were immersed in either 50 wt% aqueous sulphuric acid solution at reflux for 24 hours or in boiling dimethyl formamide (DMF) for 3 minutes. These treatments were chosen because previous work indicated that the sulphuric acid treatment would erode both the untreated virgin acrylic fibers and fibers heat treated in an inert atmosphere, but the sulphuric acid would not attack material that was completely stabilized in air. DMF, on the other hand, was found to readily dissolve virgin acrylic material, but not material heat treated for prolonged times in either air or vacuum.

Warner et al. [28] found that under diffusion-limited conditions, the formation of a two-zone morphology in the fiber existed: a dark outer mantle surrounding a light colored core. The interface between the two regions was found to move toward the center of the fiber and was associated with the diffusion of oxygen through the already-stabilized material. The increase in oxygen weight percent was found to vary with the square root of time under these conditions. Under reaction-limited stabilization conditions, Warner et al. found that a skin formed on the fiber surface, which acted as a barrier to oxygen diffusion. This oxidized material had a diffusion coefficient that was calculated as 2×10^{-12} cm^2 sec^{-1}. The diffusion coefficient of oxygen in PAN fiber at 50°C was reported as larger than this at approximately 6×10^{-10} cm^2 sec^{-1}. Because of the

factor of 300 difference between the two values, the oxidized material was regarded as having outstanding barrier properties. Once oxygen permeates the oxidized skin, however, it is relatively free to diffuse into the unreacted regions and initiate stabilization. The uptake of oxygen was found to be linear with time under theses conditions.

It has also been shown that the thermal transformation of PAN is dependent on time as well as temperature. Martin et al. [46] heat treated PAN fibers at various temperatures for various times in both nitrogen and air atmospheres. It was found that treatment at 300°C for 10 minutes yielded samples comparable with those generated at 250°C for 100 minutes. The samples treated in air demonstrated the most extreme changes. The researchers state that there is little aliphatic character left in the sample, although residual alkyl groups and C≡N exist in the nitrogen samples.

Although the exact structure of thermally oxidized PAN fiber is not known, a proposed structure by Romanova et al. [47] can be see in Figure 12.

2.2.3 Shrinkage

The application of tension during the oxidation of precursor fiber is important since it prevents polymer chains from relaxing and losing their orientation, which becomes locked-in through cross-linking and sets the basis for the preferential growth of the oriented graphene planes. Both physical and chemical changes during stabilization are affected by the presence of tension [26].

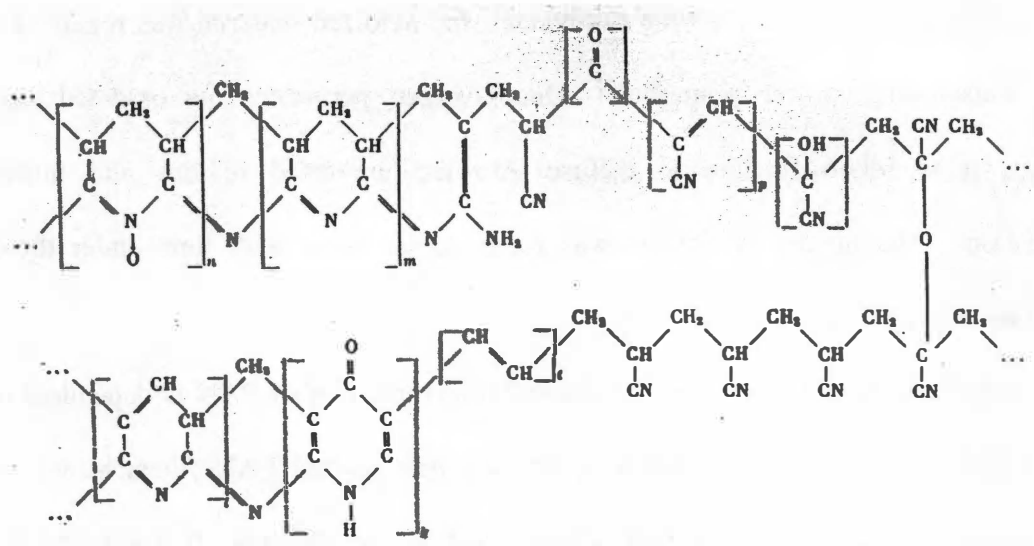

Figure 12. Proposed Structure of PAN Thermally Treated in Air.
Continuous line brackets denote the structures formed during transformation in mild conditions in large quantity and the broken line brackets in small quantity [47].

Two methods have been widely used for constraining fibers during heat treatment. In the first, the fiber is constrained to a constant length while in the second, the fiber is subjected to a constant force. When the fiber is treated under a constant length condition, a certain amount of tension, or shrinkage force, is generated as a result of the tendency of the molecular chains to coil. The extent of this coiling depends on the initial morphology of the precursor. When a constant load is applied during stabilization, the fiber could shrink if the applied load is less than the shrinkage force, extend if the applied load is greater than the shrinkage force, or remain the same length if the applied load is the same as the shrinkage force [26].

The tension generated in a homopolymer PAN fiber during its heating to 270°C while held under constant length was described by Layden [26]. A large amount of

tension was generated as the fiber was heated to 150°C, but it decreased rapidly between 150 and 250°C. The tension then rose again at 270°C before leveling off finally with time.

Warner et al. [48] studied two stabilization processes in detail: stabilization during batch processing and stabilization during continuous processing. During batch processing, two regions of shrinkage force were noted. As the fiber was heated, the tension in the fiber rose as the glass transition temperature was exceeded. This is associated with entropic recovery. At a later time, the tension rose because of chemical reactions occurring within the fibers. This rise in tension is associated with stabilization kinetics. Specifically, Warner et al. state that the shrinkage reactions can occur in the absence of an oxidizing gas, but the presence of oxygen in the atmosphere will have an accelerating effect on the rise in tension.

Jain et al. [24] state that the shrinkage stress is developed due to the tendency of the polymer chains in the disordered phase to undergo entropic relaxation. The researchers found that this tendency of the chains to coil up is greater when their orientation is higher.

Fitzer et al. [35] used an approach that separated the shrinkage into reaction shrinkage, which arises from chemical contributions, and entropy shrinkage, which is caused by a physical contribution. It was found that increasing the heating rate increased the total amount of reaction shrinkage, but the entropy shrinkage was the same in all cases. For the cases involving differing amounts of reaction shrinkage, it was found that at heating rates lower that 5°C/min, the amount of shrinkage did not change, thus it was

concluded that the mechanism of reaction shrinkage did not change. At higher heat rates, however, the reaction shrinkage started later, but it had a higher intensity, causing a higher amount of shrinkage. It was concluded that the heating rate up to the temperature at which reaction shrinkage begins should not be greater than 5°C/min.

It has been found that controlling shrinkage during stabilization plays an important role during the production of carbon fibers. Laffont et al. [49] studied a model proposed by Watt for the removal of nitrogen from stabilized PAN during the carbonization stage. According to the model proposed by Watt, neighboring graphene sheets with substituting nitrogen atoms located at graphene edges get linked to each other by elimination of nitrogen from the structure as N_2, provided that these nitrogen-bearing sites face each other [49]. Laffont et al. state that such a mechanism will be enhanced when stretching stresses are applied to the aligned ladder-polymer chains. This improves their alignment along the fiber axis and is likely to result in graphene planes that are brought closer to one another during carbonization. It was found that preventing fibers from shrinking during stabilization had three important consequences: (1) preventing shrinkage reduces pore size and pore entry-port dimensions in the precursor fiber. This slows the diffusion of gaseous oxygen and hinders subsequent oxygen atom uptake during stabilization, (2) it enhances the specific removal of nitrogen during carbonization according to Watt's mechanism by bringing the graphene sheets closer to one another. This is thought to be partially responsible for the high tensile strength of the resulting carbon fibers, and (3) it enhances the mutual alignment of the ladder-polymer chains

relative to the fiber axis. This induces a higher anisotropy in the resulting carbon fiber, increasing Young's modulus as well as the electrical and thermal conductivities.

2.2.4 Variations in Mechanical Properties

As mentioned previously, Fitzer et al. [35] found that a heating rate of 1°C/min during stabilization resulted in a maximum in the value of tensile strength for the resultant carbon fibers. These results can be seen in Figure 13. Also, a final temperature of 270°C was found to give the highest value of tensile strength of the temperatures examined.

Gupta and Harrison [50] heat treated SAF PAN precursor fibers supplied by Courtaulds Fibers, U.K. in a three-zone tube furnace. A heating rate of 1°C/min was used and the final heat treatment temperature ranged from 200 to 500°C. The fibers were constrained to a constant length condition. When fibers were stabilized in air up to approximately 314°C, a decrease in strength was observed that was due to the loss of inter-chain cohesive energy as a result of intramolecular cyclization reactions. Beyond 314°C, an increase in strength was observed due to intermolecular cross-linking reactions.

Similar trends were noticed in the values of the primary Young's modulus. For stabilization in air, the modulus fell rapidly between 215 and 267°C. This decrease was attributed to randomization of crystalline morphology. The modulus increased at higher temperatures due again to intermolecular cross-linking reactions. It was also noted that

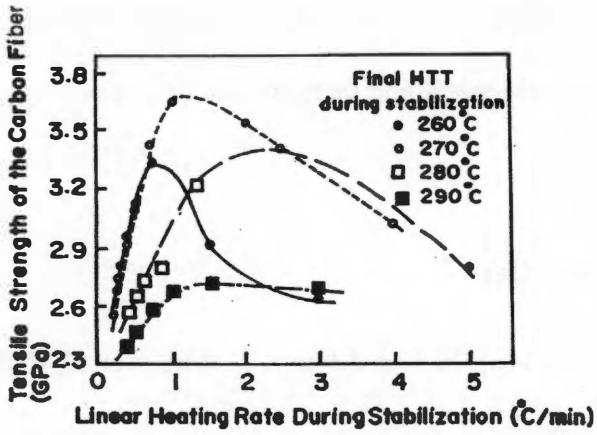

Figure 13. Effects of Heating Rate and Final Heat Treatment Temperature during Stabilization.

Fiber samples were stabilized in air environment and subsequently carbonized to get to obtain tensile strength data [35].

samples stabilized under free shrinkage conditions had consistently lower values of tensile strength and Young's modulus than samples stabilized under constant length conditions [50].

Takaku et al. [51] studied the mechanical properties of PAN precursor during heat treatment in air environment. Precursor fibers were pre-loaded with a tension of 1.4 MPa at room temperature and then heated at a rate of 1°C/min. They found that Young's modulus decreases at a fast rate with increasing temperature up to about 100°C and continues to decrease slightly up to a temperature of approximately 215°C. The contractive stress shows a maximum at 135°C and a minimum at 215°C. Coloration of the fibers was not prominent below 215°C, leading the researchers to propose that the thermo-mechanical behavior of the fibers below 215°C is due to a mechanism of a physical nature. It was theorized that the variations could be related to the two glass

transition temperatures that have been observed in PAN, one near 87°C and the other at about 140°C. This would mean that the variation of Young's modulus at temperatures up to 100°C results from the glass transitional movement of molecular chains due to the loosening of the van der Waals bonding. The transition of Young's modulus observed over the range of 100 to 215°C would be caused by the loosening of the dipole-dipole association.

Above 215°C, the tensile modulus increased with increasing temperature and reached approximately 5 GPa at 290°C. This indicated that the molecular chains in the original fibers change into a thermally stable structure in this temperature range. The contractive stress also increased with increasing temperature, reaching a peak at approximately 270°C. In studies involving the isothermal treatment of PAN fibers, it was found that Young's modulus at a fixed temperature increases with increasing treatment time and approaches a constant value at longer times [51].

Bahl and Mathur [52] heat treated Beslon fibers containing 3 percent methyl acrylate at 240°C for soak times of 100 minutes. An air flow of 3 liters per minute was maintained during the treatments. Weights ranging from 100 to 1300 grams were used to apply tension to the fibers. During the first set of experiments, the same load was applied during the heat-up period and the soak time. It was found that the strength continues to increase up to a load of 700 g. The strength then decreases sharply with a load of 850 g and then increases again and maintains a gradual fall up to the highest load applied. The Young's modulus was found to increase with load up to 700 g as well. Thereafter, it falls off to an almost constant value. During the second set of experiments, one load was used

for the heat-up period and a second load was used during the soak time. It was found that smaller loads during the heat-up period followed by larger loads during the soak time gave the best results of tensile strength and Young's modulus. Care must be taken, however, to apply the optimum load as opposed to a load that is too high. By finding the optimum load, the properties of the fibers can be upgraded significantly; it is also important to use a smaller load during the programmed heating of the fibers.

2.2.5 Thermal Behavior

Besides the strong exothermic reaction that PAN is most known for, endothermic reactions and glass transition temperatures for the polymer have also been reported in the literature. A step-like change at 100°C and an endothermic peak at 155°C were observed by Gupta and Chand. It has been observed that two glass transitions occur in unoriented PAN while a single glass transition temperature occurs in oriented fibers [27].

Bajaj et al. [27] performed a DSC comparison two PAN precursors. One precursor contained 3.2 mol% of methacrylic acid and the second contained 3.2 mol% of itaconic acid. They found a single broad melting endotherm in the precursor with methacrylic acid in the temperature range of 149-173°C with a peak at 164°C. In the case of the precursor with itaconic acid, the temperature range was shifted down to 141-196°C with a peak at 158°C. The precursor with itaconic acid also exhibited a shoulder at 149°C. When tested under high-pressure DSC, the precursor with itaconic acid exhibited two sharp melting endotherms at 155 and 168°C.

Bajaj et al. [27] also noted that copolymers with acid comonomers give two melting endotherms. The same is true for exothermic reactions as well. In the case of PAN homopolymer, the exothermic reaction takes place in a single step, while a two-step reaction is noted in copolymers.

Jain et al. [24] performed DSC measurements on precursor fibers heat treated for various times at 265°C in an air-circulating oven. A simultaneous decrease in the area under the exothermic peak and an increase in the peak width were observed. As stabilization progresses, the nitrile groups in the precursor undergo cyclization, resulting in a decrease in the intensity of the exotherm. A complete disappearance of the exotherm suggests completion of the cyclization reactions. The exotherm appeared to have completely disappeared after 106 minutes of heating at 265°C.

Bhat et al. [34] disagree with this statement, however. They note that the disappearance of the exotherm is not necessarily an indication of complete stabilization. The exotherm arises primarily from the reaction of nitrile groups, and therefore, they state that this technique fails to give information about the other reactions that are necessary for complete stabilization.

Figure 14 shows DSC data for SAF precursor, most likely a copolymer of acrylonitrile, methylacrylate, and itaconic acid wet-spun from sodium thiocyanate solution, heat treated in air atmosphere at a heating rate of 1°C/min. It is generally believe that Peak I is due to cyclization/thermal stabilization reactions. Gupta and Harrison [36] state that reactions in the crystalline part of the polymer lead to Peak II in

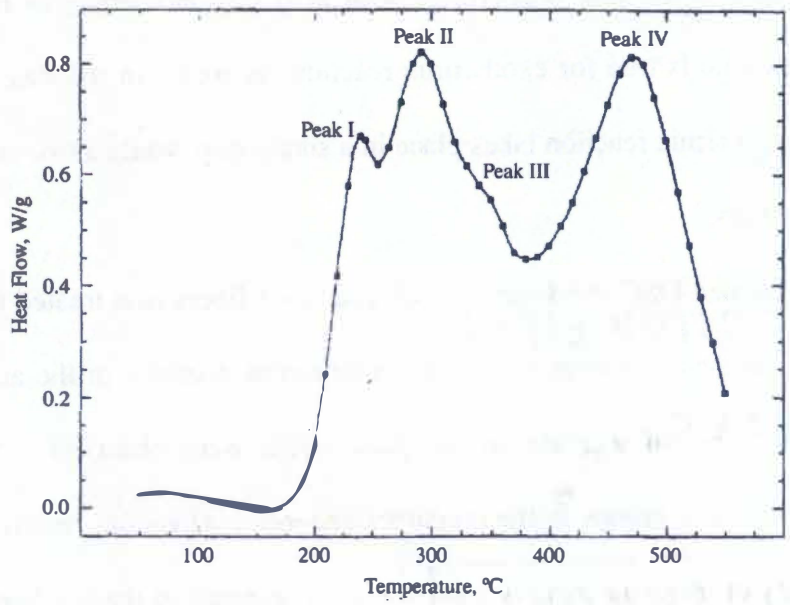

Figure 14. DSC Behavior on Heating SAF Precursor.

Precursor fiber was heat treated in air environment at a heating rate of 1°C/min [36].

the DSC curve. The origin of Peak III is not known. Oxidative degradation reactions set in at temperatures beyond 380°C, leading to the presence of Peak IV. Dunham and Edie [53] state that cyclization and dehydrogenation reactions are the source of Peak I while oxidation reactions are the source of Peak II.

Gupta and Harrison [36] found that for homopolymer PAN, the presence of a single DSC exotherm indicates only one stabilization reaction that proceeds at near equivalent rates in the crystalline and amorphous regions, both in the presence and absence of oxygen. The shape and width of the DSC peaks, as shown in Figure 15, indicates that stabilization in oxygen is mainly diffusion controlled, whereas stabilization

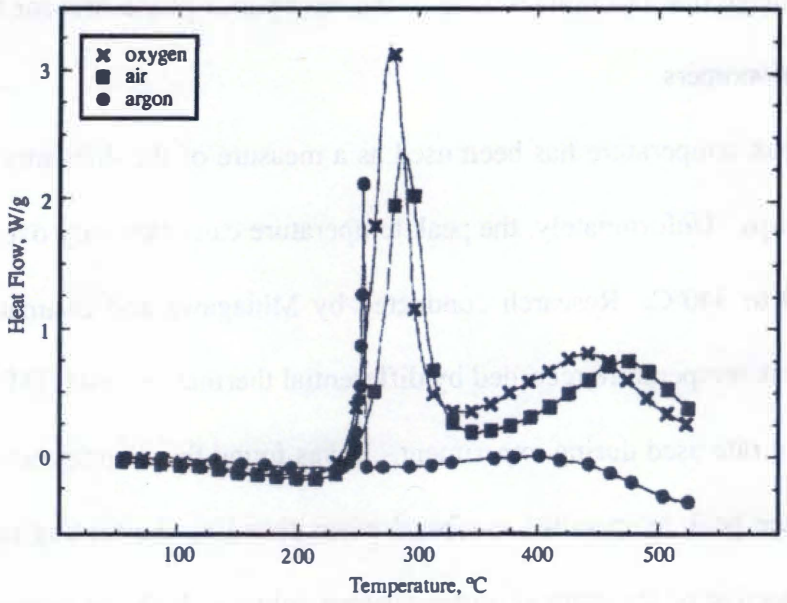

Figure 15. DSC Behavior on Heating Homopolymer PAN in Various Environments. Homopolymer PAN was heat treated in oxygen, air, and argon environments at a heating rate of 1°C/min [36].

in argon is mainly reaction controlled. For copolymer PAN, the presence of two distinct DSC exotherms for stabilization in presence of oxygen indicates the initiation of reactions in amorphous parts of the polymer and their eventual spread to the crystalline component. The researchers found that reactions initiate in the amorphous regions at lower temperatures, typically 170°C, as compared to 220°C in the homopolymer. The reason for this is the inclusion of the acid-group containing comonomers. When stabilization was carried out in the absence of oxygen, it was found that the rates of stabilization for the amorphous and crystalline regions are nearly identical, but WAXD observations and the presence of a small angle x-ray scattering (SAXS) maxima at low

temperatures seems to indicate that reactions initiate in the amorphous phase first for the acid-group containing comonomers.

The exothermic peak temperature has been used as a measure of the difficulty in reaction of nitrile side groups. Unfortunately, the peak temperature can often vary over a wide range, typically 250 to 340°C. Research conducted by Minagawa and Iwamatsu [54] has shown that the peak temperature recorded by differential thermal analysis (DTA) is dependent on the heating rate used during experiment. It was found that a temperature difference of 6 to 8°C in the peak temperature is typical when changing the heating rate from 5 to 10°C/min, irrespective of the method (homogeneous solution, bulk, or aqueous redox slurry systems) used in preparing the precursor material.

Ubbrìaco et al. [42] also studied the effect of heating rate on the thermal behavior of various PAN precursors. For all of the acrylic fibers studied, in both nitrogen and air flow, the extrapolated peak onset temperature and the maximum peak temperature are lower for a heating rate of 10°C/min than for 20°C/min. However, the heat of reaction was found to increase at the lower heating rate. Information on the heat of reaction can be seen in Figure 16. This information has been evaluated using Equations 1 and 2 from Dunham and Edie [53]:

$$\Delta H_{cyclization} = \Delta H_{nitrogen} \qquad (1)$$

$$\Delta H_{dehydrogenation} = \Delta H_{air} - \Delta H_{nitrogen} \qquad (2)$$

For the oxidized PAN fiber tested in air, the characteristic heat of reaction does not vary significantly when the heating rate changes.

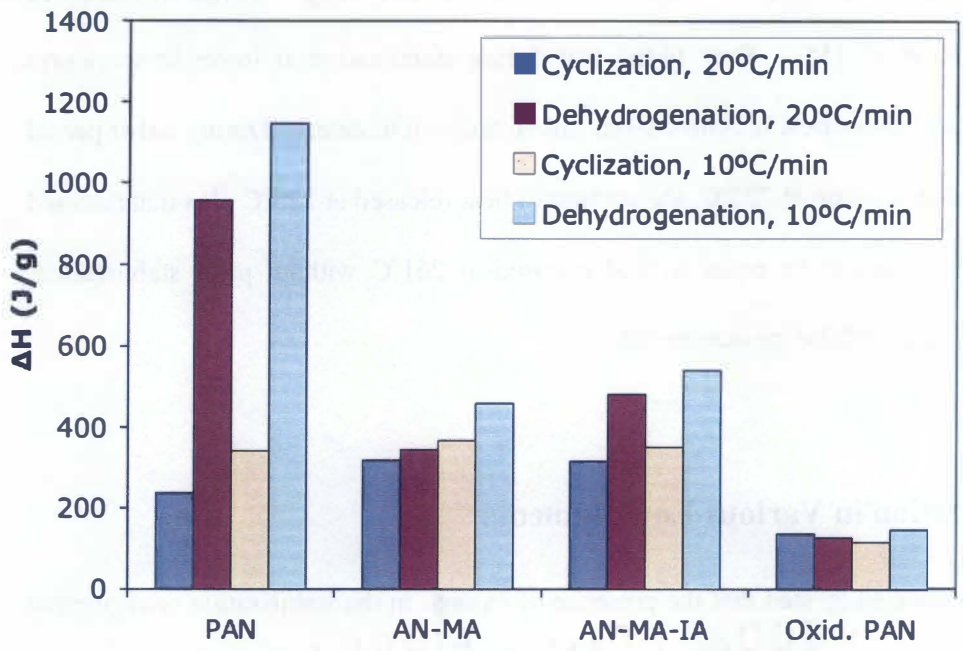

Figure 16. DSC Data for Three PAN Precursors and Commercially Oxidized PAN.

Heat of reaction data for homopolymer PAN (PAN), 93% PAN/7% MA (AN-MA), 93% PAN/6% MA/ 1% IA (AN-MA-IA), and commercially oxidized PAN fibers (Oxid. PAN) tested at heating rates of 10 and 20°C/min [42].

An interesting observation about the heat generated during stabilization was made by Peebles Jr. et al. [55]. They found that during stabilization at lower temperatures under inert conditions, heat is evolved, but can be difficult to detect. During either partial or complete stabilization at 225°C, the amount of heat released at 225°C plus that released at 261°C was found to be equal to that released at 261°C without prior stabilization, within the accuracy of the measurements.

2.3 Stabilization in Various Environments

It has been suggested that the presence of oxygen in the stabilization environment promotes the formation of double bonds or cross-links in the stabilized structure. This helps to make the stabilized structure less susceptible to cleavage during the carbonization process. However, increasing the oxygen content of the stabilizing environment does not promote a better structure for the stabilized fiber. In fact, if oxygen is added in excess, the zones of high oxygen concentration may lead to excessive cleavage when exposed to the high temperatures of carbonization [56]. Manocha and Bahl [57] state that the length of the ring sequence in stabilized PAN fibers determines the crystallite size in the final carbon fibers and thus, the mechanical properties of the carbon fibers. It was found that the ring sequence was smaller for fibers treated in oxygen atmosphere as compared to those treated in air and nitrogen atmospheres. A short ring sequence leads to poor mechanical properties in the resulting carbon fibers.

Burlant and Parsons [45] studied the gases evolved during heat treatment of PAN in both nitrogen and air environments. It was found that the rates of formation of HCN and NH_3 were the same in air as in nitrogen. They state that this indicates that oxygen does not activate the molecules at any point, a contrast to the thermal decomposition of polyvinyl chloride. They do note, however, that the polymer colors more quickly in air environment than in nitrogen environment.

Bhat et al. [34] studied the stabilization of precursor fibers heat treated in nitrogen, air, ammonia, and various combinations of these gases. They found that ammonia acts as an accelerator of stabilization reactions, reducing the time for stabilization to almost half of that required in air. This result was found to be especially true for precursors not containing an acid comonomer. It was also discovered that oxygen is essential in reaching the stabilized state. In the absence of oxygen, ammonia did not lead to complete stabilization of precursor fibers. WAXD studies performed on fibers treated in ammonia and in air/ammonia indicated that the influence of ammonia was not simply to accelerate the stabilization reactions, but also to cause the reaction paths to be different.

Peebles Jr. et al. [55] state that ammonia acts as a catalyst for the exothermic reaction of acrylonitrile polymers, but not hydrogen cyanide or an equimolar mixture of ammonia and hydrogen cyanide. From their research, it was found that under high temperature conditions, the sample turned a dark color and both ammonia and hydrogen cyanide were generated, along with an unknown yellowish condensed material. Under low temperature conditions, the samples did not turn a dark color and no condensed

material was generated. However, both ammonia and hydrogen cyanide were observed at temperatures as low as 160°C.

Romanova et al. [47] also report the presence of hydrogen cyanide and ammonia in the pyrolysis products, but they state that hydrogen cyanide makes up the bulk of the pyrolysis products. The maximum content of ammonia was not found to exceed 0.05% of the weight of the initial polymer throughout the period of thermal treatment at both 180 and 220°C. The researchers also state that the main reactions involving oxygen are the release of hydrogen cyanide, oxidative dehydrogenation, and the attachment to the nitrogen-containing structures formed in the course of thermal degradation.

Figure 6 shows DSC curves of PAN precursors stabilized in nitrogen and air environments. For a polyacrylonitrile precursor with 6% methyl acrylate and 1% itaconic acid, stabilization in air releases more heat than the same precursor stabilized in nitrogen environment. The sample stabilized in air also continues to react and release heat, going through several peaks as shown in Figure 14. The sample stabilized in nitrogen, however, finishes reacting and the heat flow returns to the baseline. A difference in the peak temperature can also be seen. Samples stabilized in air begin reacting at a lower temperature because of the inclusion of the weak acid comonomer. As stated previously, the weak acid comonomer initiates reactions in the amorphous portions of the fiber, and then the reactions spread to the crystalline regions. These reactions take place at approximately the same time and same rate during stabilization in nitrogen.

Dalton et al. [23] noted that nitrile reaction, conjugated C=C formation, and oxidation all occurred during the early stages of stabilization in air. The first two gave rise to insoluble polymer, but they state that oxidation may have lead to chain scission.

Gupta and Harrison [36] measured the shrinkage force during stabilization for heat treatment in argon, air, and oxygen. Up to 90°C, the stress relaxes; then between 90 and 150°C, the stress increases. It was found that the stress rise beyond 150°C was highly dependent on the environment used during heat treatment. Heating in the presence of oxygen was found to produce a larger decay in stress between 150 and 200°C. It was also noted that the absolute values of thermal stress at temperatures above 200°C for a given environment were independent of the amount of pre-tension. As the fibers are further heated, it is noted that the thermal stress goes through a maximum at approximately 250°C and then decreases to zero upon further heat treating in argon environment. As the treatment temperature is increased beyond 320°C in air and oxygen environments, oxidative degradation reactions set in and the stress rises rapidly until tow breakage occurs.

Chapter 3

Stabilization Versus Oxidation

Stabilization and oxidation are sometimes referred to interchangeably since the stabilization of PAN precursor is carried out in air environment in a commercial setting. This is oftentimes acceptable, as long as the meaning is made clear to the reader. The two should not be mistaken as the same process, however. Important distinctions separate stabilization from oxidation, as outlined below.

Stabilization is the process where chemical reactions take place during heat treatment to convert the precursor fiber into a thermally stable form suitable for high-temperature carbonization.

Oxidation is the process where oxygen in the treatment environment reacts with the precursor fiber, creating an oxidized material on the outer surface of the fiber that slowly grows in toward the center as oxygen diffuses into the fiber.

Using these definitions, the differences between stabilization and oxidation are made clear. Stabilization of PAN precursor can take place in any environment so long as sufficient heat is applied to initiate the chemical reactions necessary for the fiber to become infusible. The presence of oxygen is not required for stabilization to take place; stabilization can be carried out in inert environments and vacuum just as well as it can be carried out in air and pure oxygen environments. Oxidation, by definition, can only take place in oxygen-containing environments. Oxidation also takes place at all temperatures, not just those required to initiate stabilization. An important consequence of the

differences between stabilization and oxidation is that it is possible to have a fully stabilized precursor fiber that is not fully oxidized.

This is not to imply that an oxygen-containing environment is not important in the stabilization of PAN precursor. In 1961, Shindo was the first to recognize the importance of an oxidative heat treatment prior to the carbonization and graphitization steps to improve the carbon yield from PAN [1]. Since that time, it has been suggested that the presence of oxygen in the stabilization environment promotes the formation of double bonds or cross-links in the stabilized structure. This helps to make the stabilized structure less susceptible to cleavage during the carbonization process. However, increasing the oxygen content of the stabilizing environment does not promote a better structure for the stabilized fiber. In fact, if oxygen is added in excess, the zones of high oxygen concentration may lead to excessive cleavage when exposed to the high temperatures of carbonization [56]. Manocha and Bahl [57] state that the length of the ring sequence in stabilized PAN fibers determines the crystallite size in the final carbon fibers and thus, the mechanical properties of the carbon fibers. It was found that the ring sequence was smaller for fibers treated in oxygen atmosphere as compared to those treated in air and nitrogen atmospheres. A short ring sequence leads to poor mechanical properties in the resulting carbon fibers.

The importance of oxygen in the stabilization environment can be summarized as follows: (1) the presence of oxygen in the stabilizing atmosphere promotes the initiation of cyclization, and this initiation is involved with chain scission and the formation of initiator sites; (2) as the temperature is raised, chain scission, the number of initiator sites,

and the overall kinetics of the stabilization process are increased; (3) oxygen participates in a number of cross-linking reactions, i.e., at the chain end, after scission, and on the polymer backbone; (4) dehydrogenation reactions, promoted by an oxidative environment, lead to a conjugated and planar backbone structure, which combined with cyclization, yields a pre-structure of sheet-like character capable of being stacked, a preferred arrangement for subsequent carbonization; and (5) the combined effects of chain scission and the tacticity of PAN (random atactic) preclude long segments of cyclized chains from being formed [3].

Chapter 4
Experimental Procedure

4.1 Materials

Commercially-available, low-count tow PAN precursor was chosen for the stabilization experiments. The fiber diameter of the precursor is 12.7 μm with a standard deviation of 0.6 μm. The specific chemical composition and comonomer additions in the precursor are not known. Samples obtained by heat treating this commercial precursor will be referred to as conventionally-treated samples.

In order to compare the progression of stabilization and oxidation reactions in the internally heat-treated samples, commercially heat-treated samples were obtained from a separate source. The samples included precursor material, fully oxidized material, and material taken from various positions in the commercial process. The treatment temperatures and times for the samples are not known, but bulk density measurements were made in order to separate and identify the samples for purposes of comparison. A listing of various properties can be found in Table 4 for the commercial and conventional precursors. Table 5 gives a listing of commercially-treated samples obtained and their bulk densities.

Table 4. Properties for the Commercial and Conventional Precursors.

Property	Commercial	Conventional
Fiber diameter (μm)	12.36±0.53	12.72±0.64
Density (g/cc)	1.200±0.004	1.181±0.004
ΔH_{250} (J/g)	123.49±6.58	77.94±1.66
ΔH_{300} (J/g)	1300.65±14.51	1226.82±25.04

Table 5. Density Information for Commercially-Treated Samples.

Sample ID	Bulk Density (g/cc)
Precursor	1.200
Sample 1	1.235
Sample 2	1.288
Sample 3	1.325
Fully Stabilized	1.384

4.2 Heat Treatment of Precursor Fibers

A programmable oven was used during heat treatment of conventionally-treated samples because of the need to control both heating rate and the final heat treatment temperature. Figure 17 shows a schematic of the general heating profile used during the heat treatments. Precursor fiber was placed in the oven at room temperature, indicated by point A. A heating rate of 5°C/min was then used to heat the sample to the equilibration temperature of 90°C at point B. An equilibration time of ten minutes was then imposed between points B and C to insure that both the oven and precursor fiber sample began treatment at the same temperature. The precursor fiber then experienced a heating rate of 1°C/min up to the soak temperature at point D. The heating rate of 1°C/min was chosen after the research of Fitzer et al. [35], who showed that a heating rate of 1°C/min during stabilization resulted in a maximum in tensile strength in the resulting carbon fibers. This is shown graphically in Figure 13. Variable soak times were imposed on the fiber samples between points D and E. Once treatment was over, the fiber samples were quenched to room temperature at point F.

It is important to note that some fiber samples were given zero minute soak times. This means that once the samples reached point D, they were quenched to room temperature without experiencing any soak time, though they were still heat treated during the ramp-up time. Also, the precursor fiber was wound around a glass frame and tied at the ends to impose a constant length constraint during heat treatment.

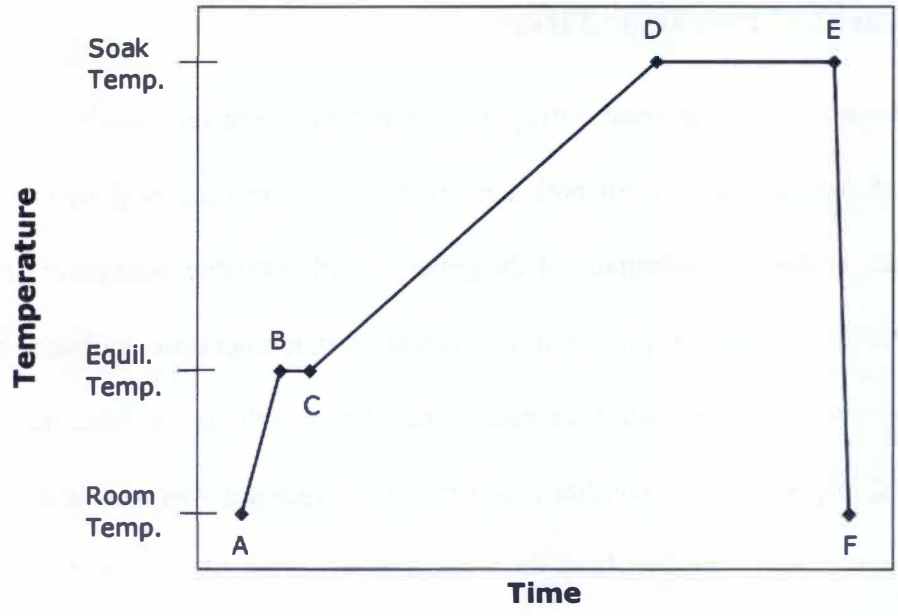

Figure 17. Schematic Heating Profile.

During the heat treatments, the treatment environment, atmospheric pressure, soak temperature, and soak time were all varied. Fiber samples were treated in nitrogen, air, and oxygen environments. The atmospheric pressure ranged from 0.5 to 5 atmospheres absolute pressure. The soak temperature varied from 215 to 290°C, and the soak time ranged from 0 to 1440 minutes (24 hours). A detailed listing of sample parameters varied during heat treatment can be found in Tables 6, 7, and 8.

In order to study all of these variables successfully, it was necessary to construct a heat treatment system in which treatment environment, atmospheric pressure, soak temperature, and soak time could all be varied. A schematic of the heat treatment system can be seen in Figure 18. If the top portion of the schematic is followed for heat

Table 6. Treatment Conditions for Samples Heat Treated in Nitrogen Environment.

Pressure (atm)	Soak Temp. (°C)	Soak Time (min)
1	215	60
1	220	0,60
1	230	60
1	235	0, 60
1	250	0, 60
1	270	0, 60

Table 7. Treatment Conditions for Samples Heat Treated in Air Environment.

Pressure (atm)	Soak Temp. (°C)	Soak Time (min)
0.5	230	0, 60
1	160	120, 360, 1440
1	180	120, 360, 1440
1	215	60
1	220	0, 60
1	230	60
1	235	0, 30, 60, 120, 180, 240
1	250	0, 15, 30, 60, 125, 180, 360, 960, 1440
1	270	0, 15, 30, 45, 60, 120
1	290	0, 15, 30, 45, 60, 120
2	220	0, 60
2	235	0, 60
2	250	0, 60
3	215	60
3	230	60
3	235	0, 60
3	250	0, 60
5	230	0, 60

Table 8. Treatment Conditions for Samples Heat Treated in Oxygen Environment.

Pressure (atm)	Soak Temp. (°C)	Soak Time (min)
1	215	60
1	220	0, 60
1	230	60
1	235	0, 60
1	250	0, 60
2	220	0, 60
2	235	0, 60
2	250	0, 60
3	235	0, 60
3	250	0, 60

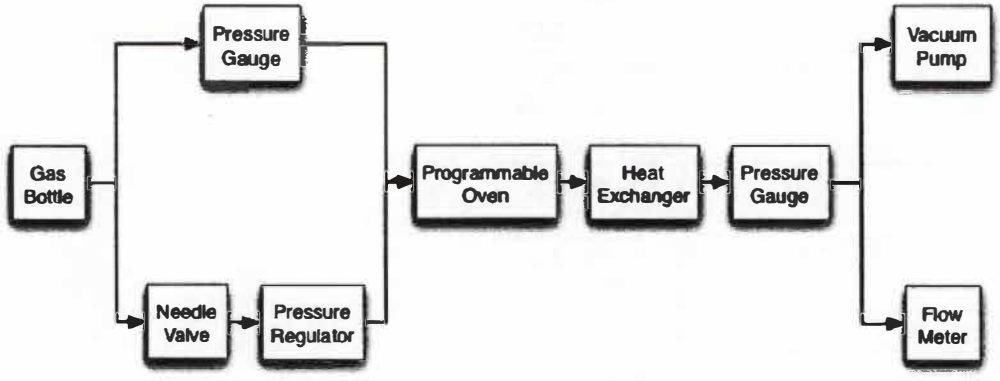

Figure 18. Schematic of Heat Treatment System Used for Stabilization Experiments.

treatment, pressures less than 1 atmosphere can be applied to the fiber sample. If the bottom portion of the schematic is followed, pressures up to 5 atmospheres can be applied to the system. The gas bottle at the start of the system can be changed between nitrogen, air, and oxygen, depending on the environment required. The programmable oven allows for the soak temperature and soak time to be varied as required by the heat treatment.

The precursor fiber sample was wound around a small glass frame and tied at the ends in order to impose a constant length constraint during heat treatment. For samples requiring a specific environmental gas or pressure, a small environmental chamber was placed in the programmable oven to hold the precursor fiber sample during heat treatment. This reduced the time required to purge the system with the environmental gas being used for treatment.

At the beginning of the heat treatment, high gas flow rates in excess of 2 liters per minute were used to purge the system to insure that only the environmental gas was present for heat treatment. Also, a sufficient length of copper tubing was coiled inside the programmable oven to insure that the environmental gas was at the treatment temperature before entering the environmental chamber. During the equilibration time, the gas flow rate was adjusted to 0.5 liters per minute and left at that level for the remainder of the treatment. Also during the equilibration time, atmospheric pressure was applied as desired for the treatment.

After the fiber samples were heat treated, four experimental techniques were used to examine the samples. The techniques were (1) wide-angle x-ray scattering, (2) density

gradient column, (3) differential scanning calorimetry, and (4) scanning electron microscopy.

4.3 Wide-Angle X-Ray Scattering

Pinhole wide-angle x-ray scattering (WAXS) patterns were made of the heat-treated fiber samples using an image plate system. The fiber samples were aligned parallel to one another on a fiber sample holder. CuKα radiation was used with an exposure time of one hour, an accelerating voltage of 45kV, and an accelerating current of 0.66 mA.

Once the WAXS patterns were made, they were scanned into a computer system. A WAXS pattern for the PAN precursor used for the stabilization experiments can be seen in Figure 19. Because of the difficulty in observing minute changes brought on by heat treatment, the software program Polar® was used to evaluate the WAXS patterns. Polar® allowed for equatorial slices to be taken from each sample pattern for comparison purposes. Figure 20 shows a sample equatorial slice taken from the WAXS pattern shown in Figure 19. Peak positions were calibrated with lanthanum boride (LaB_6) and all patterns were adjusted to the intensity of the PAN precursor sample to correct for differences in the amount of material examined.

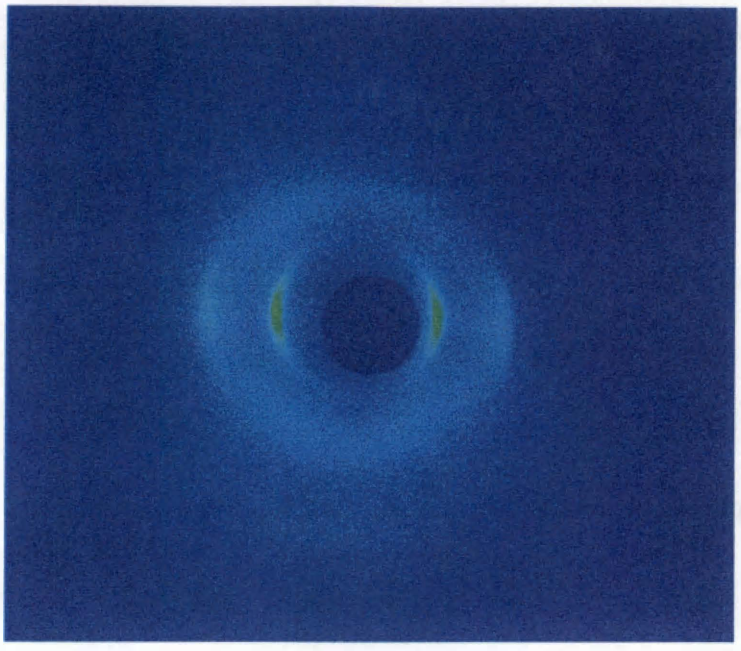

Figure 19. Wide-Angle X-Ray Scattering Pattern of PAN Precursor.

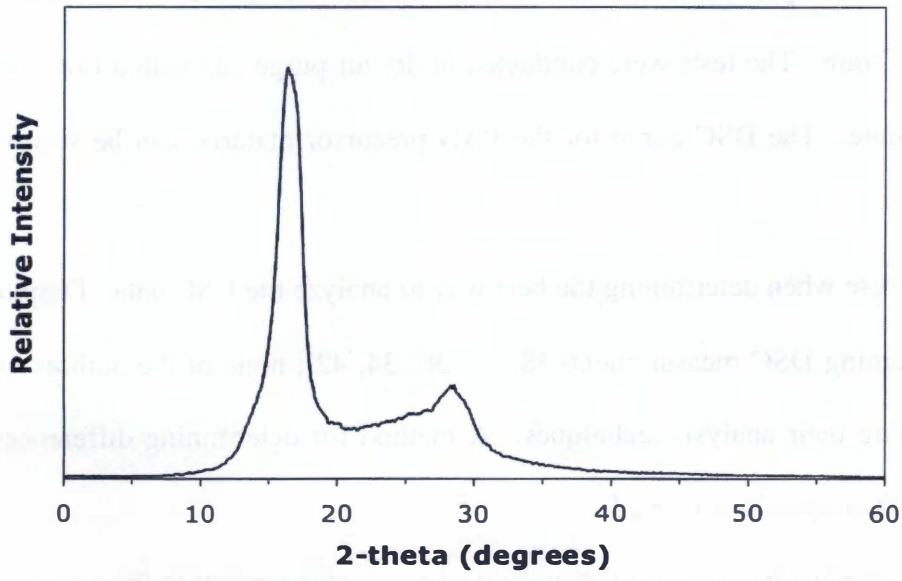

Figure 20. Equatorial Slice from WAXS Pattern of PAN Precursor.

4.4 Density Gradient Column

Two density gradient columns (DGC) were prepared to test the density of heat-treated samples. Solutions of water and sodium bromide (NaBr) were used to make columns ranging from 1.2000 to 1.4000 g/cc. Column 1 had a density range of 1.2000 to 1.3250 g/cc and column 2 had a density range of 1.3000 to 1.4000 g/cc. The tolerance of the calibration beads used was ±0.0002 g/cc. The use of two columns allowed for the densities of the heat-treated samples to be determined within ±0.004 g/cc.

4.5 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) experiments were conducted on heat-treated samples. The temperature range for the experiments was 100 to 350°C with a heating rate of 20°C/min. The tests were conducted in dry air purge gas with a flow rate of 100 mL per minute. The DSC curve for the PAN precursor material can be seen in Figure 21.

Difficulty arose when determining the best way to analyze the DSC data. Despite the literature concerning DSC measurements [8, 27, 30, 34, 42], none of the authors go into detail concerning their analysis techniques. A method for determining differences between heat-treated samples was needed.

Ideally, the baseline used in calculating heat of reaction is tangent to the curve on both sides of the peak under consideration. As stated before, however, the heat of

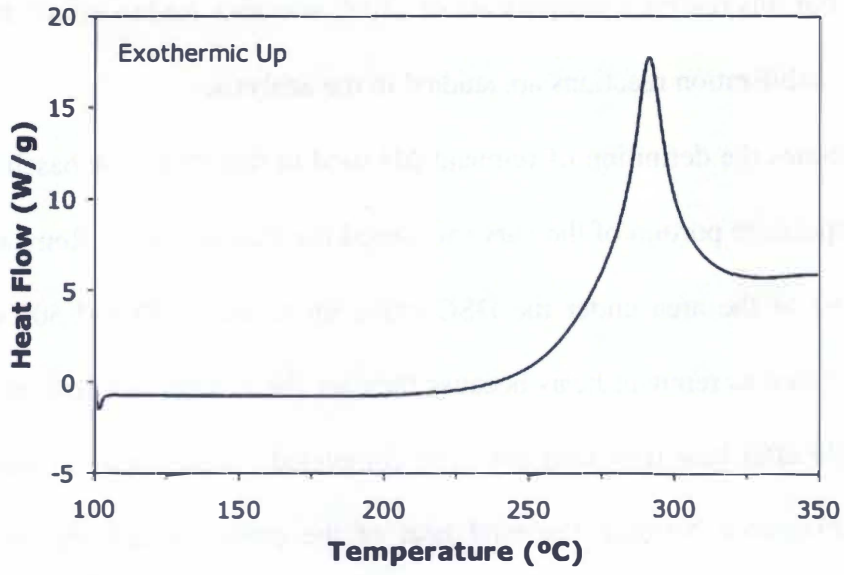

Figure 21. DSC Scan of Conventional PAN Precursor.

PAN precursor was tested in air purge gas with a flow rate of 100 mL per minute over the temperature range of 100 to 350°C at a heating rate of 20°C/min.

reaction does not return to the baseline during heat treatment in air environment. Thus, the baseline used for calculation can only be tangent to the left portion of the curve. Temperatures of 250 and 300°C were chosen as the upper limits of integration. It has been reported that Peak I is present due to cyclization and thermal stabilization reaction in the precursor material [36], hence a temperature of 300°C was chosen to isolate Peak I as best as possible.

It should be noted that a temperature of 300°C is at the upper limit of temperatures generally used for oxidative stabilization, as shown in Figure 2. Because of this, it is possible that around 300°C, carbonization reactions may begin and affect the remnant

heat values obtained. For this reason, a temperature of 250°C was also used to insure that only thermo-oxidative stabilization reactions are studied in the analysis.

Figure 22 illustrates the definition of remnant ΔH used in this study. A baseline tangent to the low-temperature portion of the curve was used for measurement. Remnant ΔH was then calculated as the area under the DSC curve up to both 250 and 300°C. These quantities are defined as remnant heats because they are the exothermic heats still remaining in the sample after heat treatment has been completed. Stated another way, remnant heat is the difference between the total heat of the precursor and the heat expelled during heat treatment.

4.6 Scanning Electron Microscopy

Heat-treated samples were examined using scanning electron microscopy (SEM). Initially, fibers were etched in 50 wt% aqueous sulphuric acid solution at reflux for 24 hours after Warner et al. [28]. As stated previously, this treatment is reported to dissolve both the untreated virgin acrylic material and material heat treated in an inert environment while leaving material completely stabilized in an oxygen-containing environment unaffected. This means that stabilized material that was not oxidized during heat treatment will be dissolved while stabilized material that was oxidized will not be dissolved. An example of this etching treatment can be seen in Figure 23. While this technique produces clear evidence for the development of a two-zone morphology during

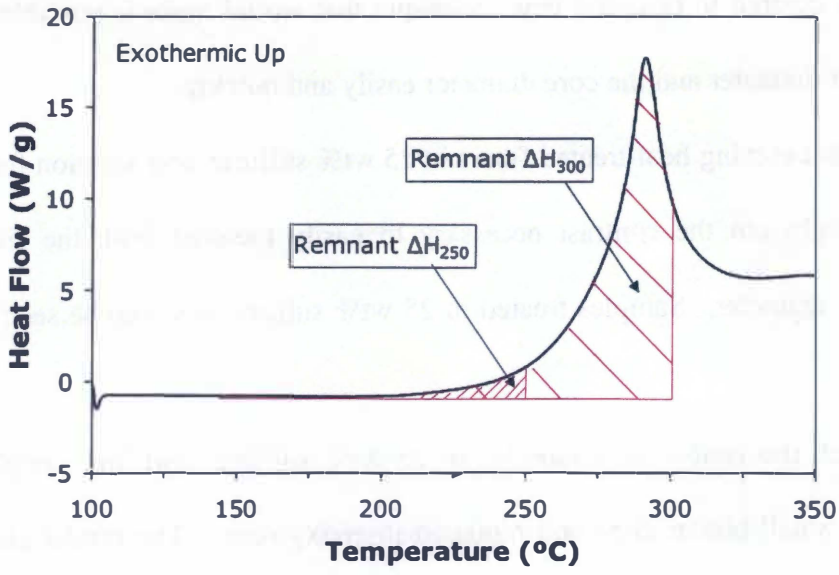

Figure 22. Illustration for Calculation of Remnant Heat.

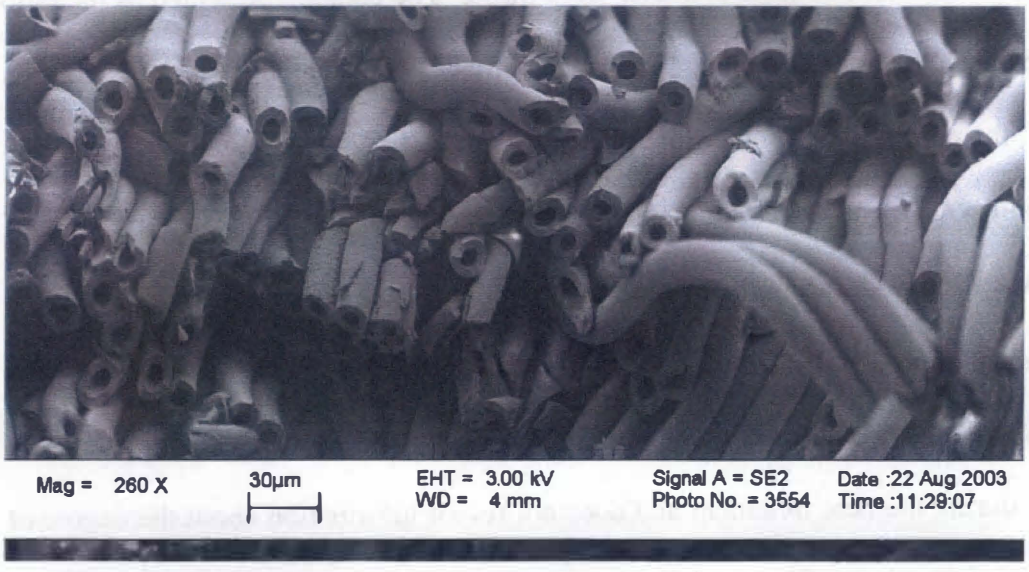

Figure 23. 50 wt% Sulfuric Acid Treatment.

PAN precursor fibers were heat-treated isothermally in air environment at atmospheric pressure at a temperature of 250°C for 60 minutes. The fibers were then etched in 50 wt% sulfuric acid at reflux for 24 hours.

heat treatment, it was desired to design a new technique that would make it possible to measure both the fiber diameter and the core diameter easily and quickly.

It was found that etching heat-treated fibers in 25 wt% sulfuric acid solution for 5 minutes at 96°C brought out the contrast necessary to easily measure both the fiber diameter and the core diameter. Samples treated in 25 wt% sulfuric acid can be seen in Figure 24.

In order to etch the heat-treated samples in 25 wt% sulfuric acid, the samples were first placed into small binder clips and mounted in epoxy resin. The binder clips insured that the fiber samples stayed vertically aligned while the epoxy cured. The samples were then polished using metallographic techniques to a finish of 0.05 μm.

Once the samples were etched, they were coated in gold and measurements of both the core diameter and fiber diameter were made. The data are presented as the ratio of core diameter to fiber diameter. This means that if core diameter/fiber diameter is equal to 1, the core is equal to the fiber diameter and the fibers were dissolved away due to the etching treatment. A core diameter/fiber diameter value of 0 means that none of the fiber was dissolved during the etching treatment and the fiber was uniform across the cross-sectional area.

It should also be noted that this technique is solely a measure of the oxidation that took place during the heat treatment and does not reveal information about the degree of stabilization of the fibers. This technique also does not reveal information on the oxygen content in the observed skin region. It is possible that a certain level of oxygen content is

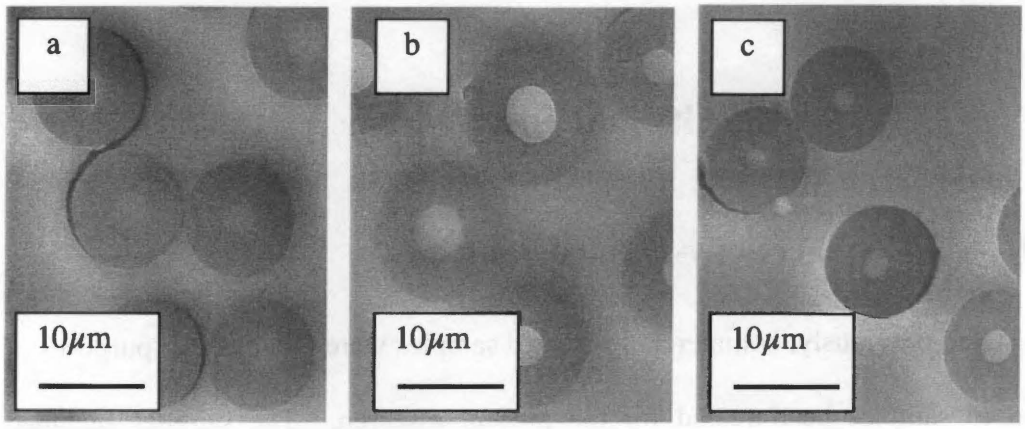

Figure 24. 25 wt% Sulfuric Acid Treatment.

PAN precursor fibers were heat-treated as described previously in air environment at atmospheric pressure at a soak temperature of 250°C for soak times of (a) 60 minutes, (b) 120 minutes, and (c) 180 minutes. The fibers were then etched in 25 wt% sulfuric acid at 96°C for 5 minutes.

needed for the fibers to survive the acid treatment, which would mean that material with an insufficient level of oxidation would also be eroded by the acid treatment.

Chapter 5

Results and Discussion

5.1 Analysis of Commercially-Treated Samples

As stated previously, commercially-treated samples were obtained for purposes of comparison to samples heat treated for the present research. The samples included precursor material, fully stabilized material, and material from various positions in the stabilization process. The treatment temperatures and times are unknown for the samples. Because of this, the samples' bulk densities were used to identify them. Table 5 gives density information for the samples. In order to compare the commercial samples to the samples heat treated in this work, the commercial samples were examined using the same techniques as those employed to study the heat-treated samples.

The changes in x-ray scattering patterns that occur in commercially-treated samples are shown in Figure 25. In all figures depicting WAXS data, the scan of the precursor is included for purposes of comparison. Additionally, the sample scans have been purposely offset in order to better show data from multiple scans. In Figure 25, initially the precursor contains two crystalline peaks at approximately 17 and 27 degrees two-theta. As stabilization of the precursor material progresses, the crystalline peaks lose intensity. By the completion of stabilization, the precursor material has been converted into the "Fully Stabilized" material, which has an essentially amorphous morphology, but a barely emerging peak can be seen at approximately 25° 2θ, which is the location of the (002) reflection in carbonized fiber.

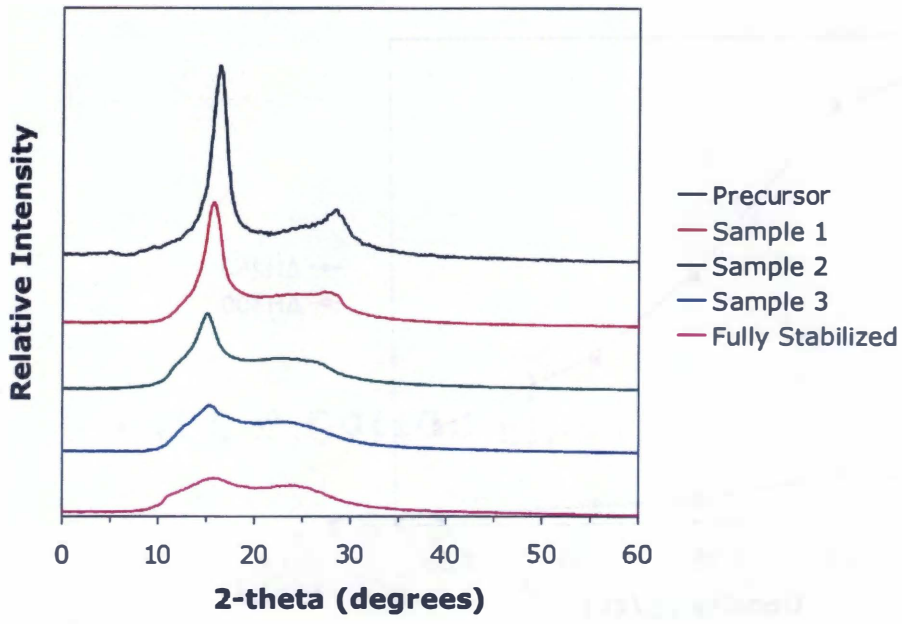

Figure 25. WAXS Scans of Commercially-Treated Samples.

The thermal behavior for the commercially-treated samples is shown in Figure 26. As the stabilization treatment progresses, the remnant heat of the fibers decreases monotonically, within the error bars for measurements, for integrations up to 250 and 300°C.

Results from the SEM analysis are shown in Figure 27. The precursor material and material with densities of 1.235 and 1.288 g/cc have a value of 1, indicating that the samples dissolved uniformly during the 25% sulfuric acid treatment described previously (96°C for 5 to 10 minutes). Once the stabilization treatment has progressed far enough for the sample density to reach 1.325 g/cc, a two-zone morphology is observed, due to the formation of a fully oxidized skin on the fiber surface.

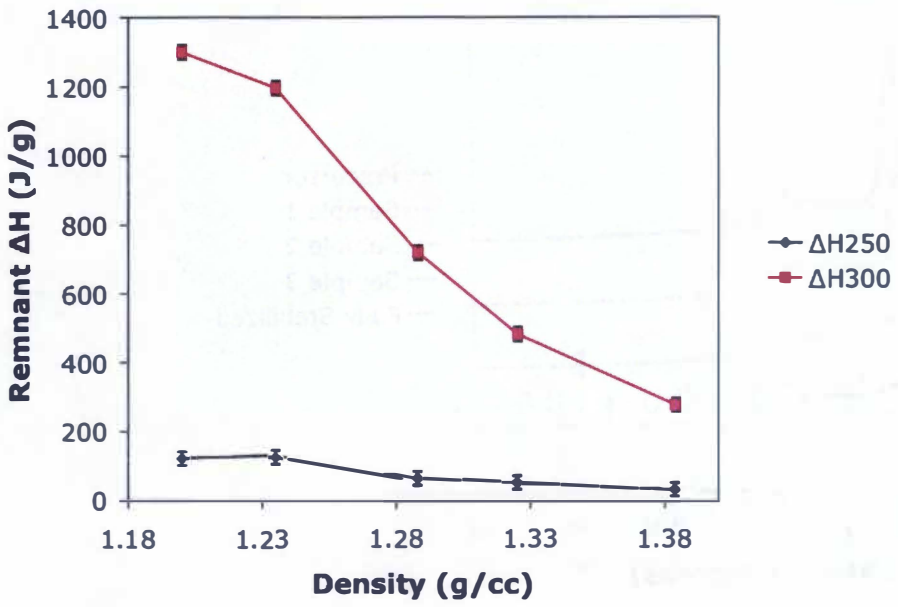

Figure 26. DSC Results of Commercially-Treated Samples.

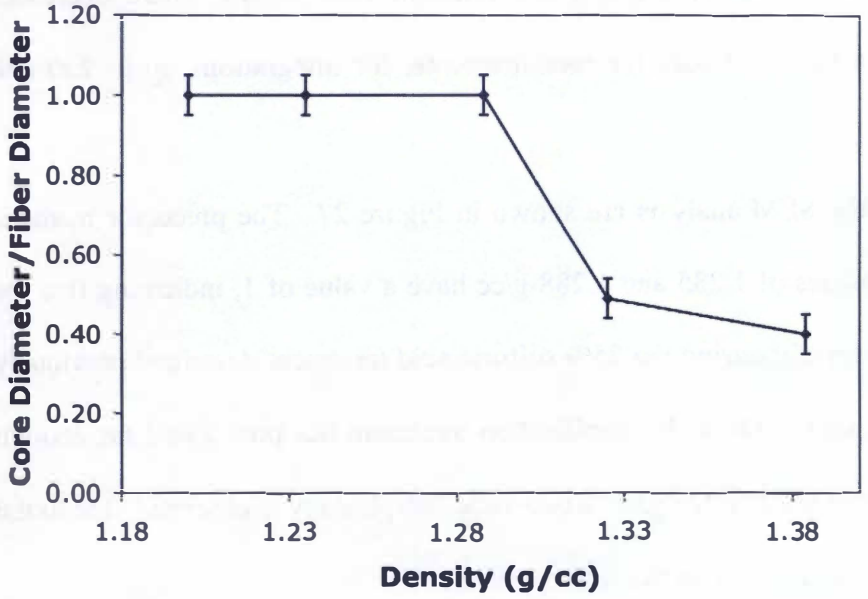

Figure 27. SEM Results of Commercially-Treated Samples.

Surprisingly, the "Fully Stabilized" sample also exhibited a two-zone morphology. This is shown in SEM micrographs presented in Figure 28. The sulfuric acid treatment used for examination of fiber cross-sections was chosen because of its ability to remove material with an insufficient level of oxidation, including virgin material and material heat treated in inert environment. Since the acid treatment attacked the core of the "Fully Stabilized" sample, it is clear that this material has not been fully chemically oxidized.

5.2 Analysis of Conventionally-Treated Samples

5.2.1 Effect of Temperature

The effect of temperature was studied primarily by examining samples heat treated in air environment at atmospheric pressure with a soak time of 0 minutes. These samples were heat treated at a heating rate of 1°C/min from 90°C to the selected soak temperature. The samples were then removed from the oven and quenched into air at room temperature. While the samples received essentially no treatment time at the soak temperature, it is noted that they still received heat treatment during the ramp-up time.

The changes that occurred in the x-ray patterns during the heating of the precursor are shown in Figure 29. Around 220°C, the peak at approximately 17° 2θ undergoes sharpening as reported by Jain and Abhiraman [22] and Pinghua et al. [25]. After the

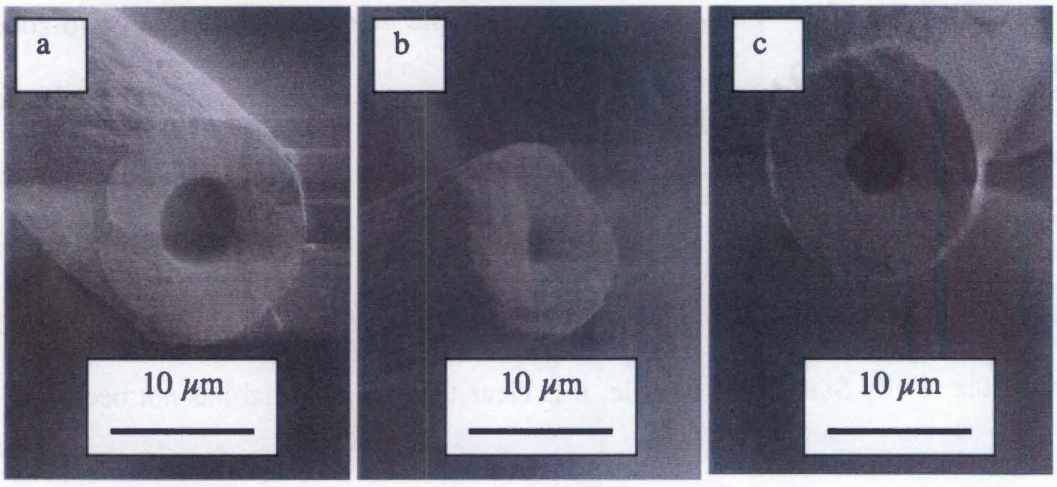

Figure 28. SEM Micrographs of Commercial "Fully Stabilized" Fiber.

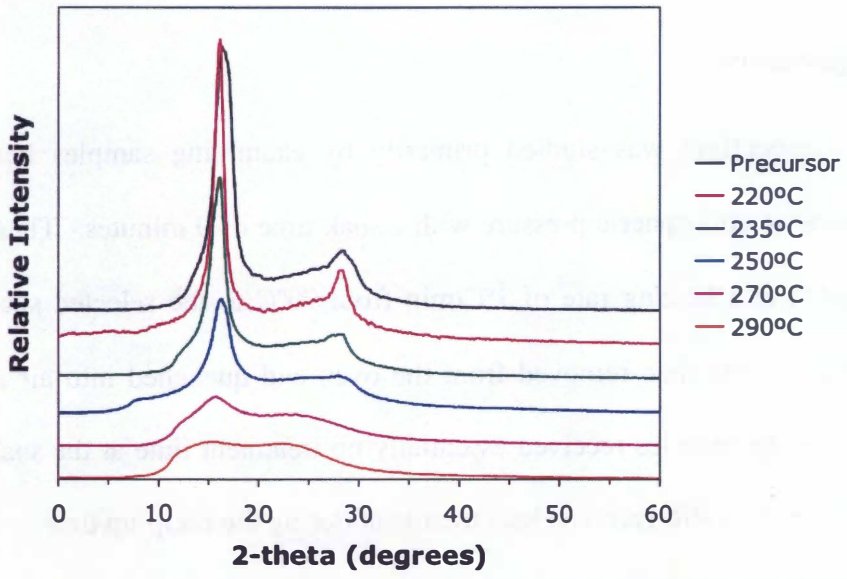

Figure 29. WAXS Scans of Samples Treated in Air for 0 minutes Soak Time.

Precursor fiber samples were heat treated in air environment at atmospheric pressure as described previously. The soak time was 0 minutes and the soak temperatures are indicated.

initial sharpening of the peak, the peaks lose intensity and broaden until an essentially amorphous morphology is achieved at a soak temperature of 290°C. Also at 290°C, a small peak at approximately 25° 2θ can be seen. As stated previously, this is the location of the (002) reflection in carbonized fiber.

As the morphology of the samples transitions from a semi-crystalline to an amorphous morphology, the density is increased. As the soak temperature is increased, the density of the samples increases in an essentially linear manner. This linear dependence on soak temperature is shown in Figure 30. The density of the sample treated at 290°C for 0 minutes soak time is not included. This is due to the fact that this sample's density was outside of the measurement range provided by the density gradient columns used. Because the highest density that could be measured in the density gradient column was 1.40 g/cc, we can say that the sample heated to 290°C had a density greater than 1.40 g/cc. A listing of all samples whose densities could not be determined because they were outside of the DGC's range is given in Table 9.

The remnant heat measured in the samples after heat treatment decreases monotonically. As the soak temperature is increased, the remnant heat measured at both 250 and 300°C decreases. This relationship is shown in Figure 31.

Measurements on the oxidation that took place during heat treatment of fibers are shown in Figure 32. The results appear to be much the same for the conventionally-treated samples as for samples treated commercially. At lower soak temperatures, the oxidation that has taken place is insufficient to allow the fiber to withstand the acid

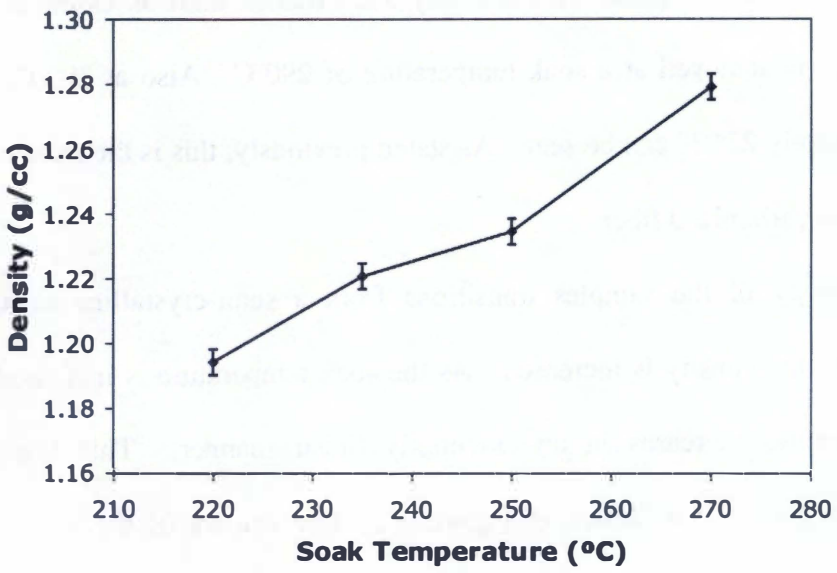

Figure 30. DGC Results for Samples Treated in Air for 0 Minutes Soak Time.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak time was 0 minutes.

Table 9. Samples with Densities Outside of Measurement Range.

Sample	Environment	Soak Temp. (°C)	Soak Time (min)	Pressure (atm)
Conventional Precursor	--	--	--	--
1	Air	160	120	1
2	Air	160	360	1
3	Air	160	1440	1
4	Air	180	120	1
5	Air	250	360	1
6	Air	250	960	1
7	Air	250	1440	1
8	Air	270	30	1
9	Air	270	45	1
10	Air	270	60	1
11	Air	270	120	1
12	Air	290	0	1
13	Air	290	15	1
14	Air	290	30	1
15	Air	290	45	1
16	Air	290	60	1
17	Air	290	120	1
18	Air	250	60	3
19	Oxygen	250	60	1
20	Oxygen	235	60	2
21	Oxygen	250	60	2
22	Oxygen	235	60	3
23	Oxygen	250	60	3

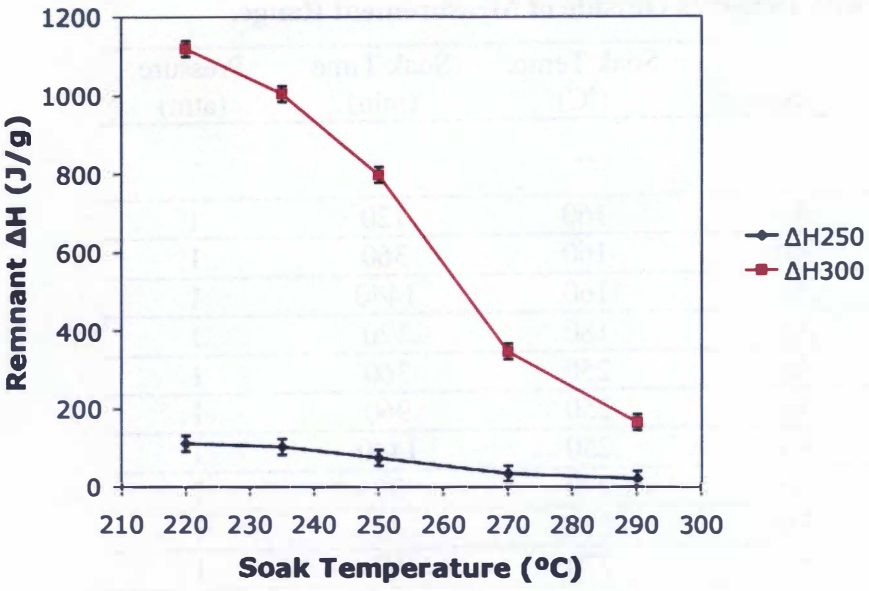

Figure 31. DSC Results for Samples Treated in Air for 0 Minutes Soak Time.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak time was 0 minutes. Results are given for both ΔH_{250} and ΔH_{300}.

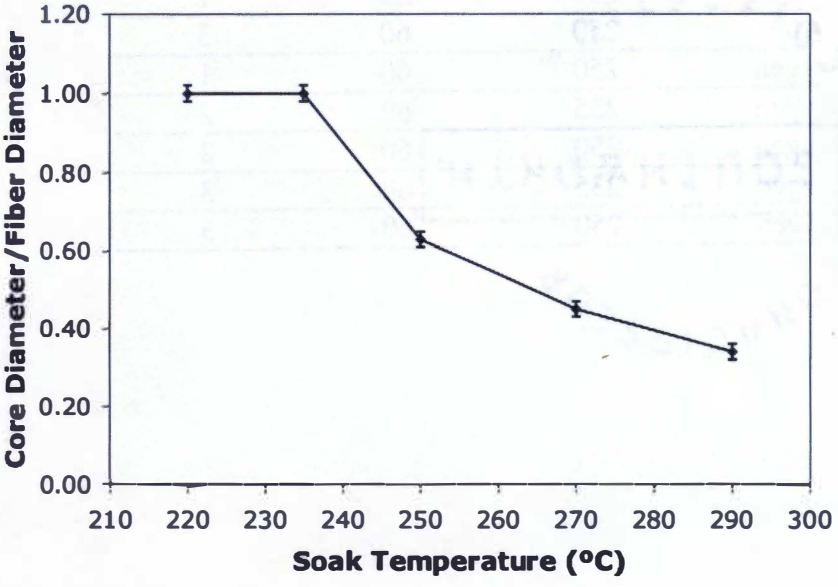

Figure 32. SEM Results for Samples Treated in Air for 0 Minutes Soak Time.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak time was 0 minutes.

treatment. However, as the soak temperature is increased, the oxidized layer grows thicker and the acid treatment is unable to dissolve the fiber samples completely.

In conclusion, as the soak temperature is increased in air environment, the fiber samples lose crystallinity. The density of the fiber samples increases in an almost linear fashion while the remnant heat remaining in the samples decreases monotonically. The amount of material that was fully oxidized during treatment also increases as soak temperature is increased, although the relationship is not linear with respect to soak temperature.

5.2.2 Effect of Time

The effect of time was studied primarily by extending the soak times for samples heat treated in air environment at atmospheric pressure at the mentioned soak temperatures. When the samples reached the soak temperature after being heated from 90°C at 1°C/min, they were allowed to stay at the soak temperature for the selected soak times.

WAXS scans for samples heat treated at 235, 250, 270, and 290°C are shown in Figures 33, 34, 35, and 36, respectively. As the soak time is increased, the intensity of the crystalline peaks decreases and an amorphous morphology is obtained. The time required to obtain an amorphous morphology becomes much shorter as the soak temperature is increased. As seen in Figure 36, the new peak at approximately 25° 2θ gains intensity as the soak time is increased.

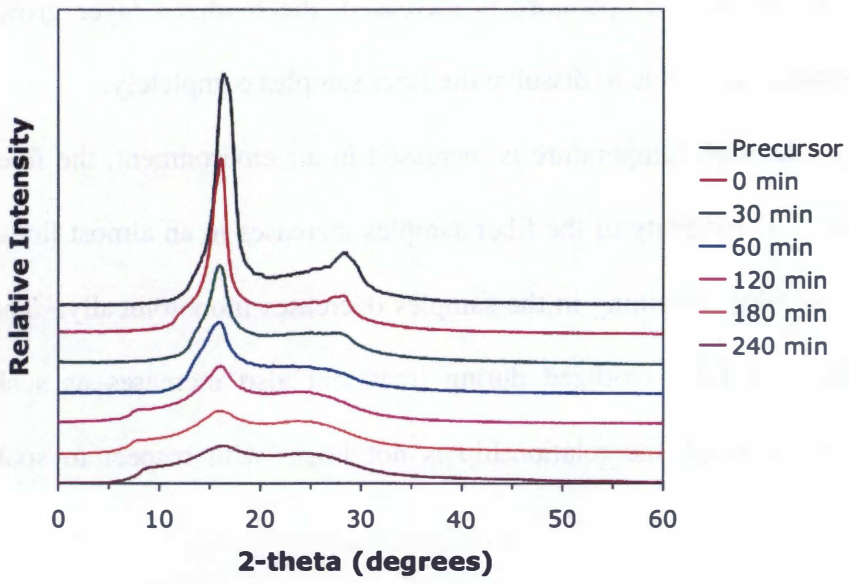

Figure 33. WAXS Scans for Samples Treated in Air at 235°C.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperature was 235°C and the soak times are indicated.

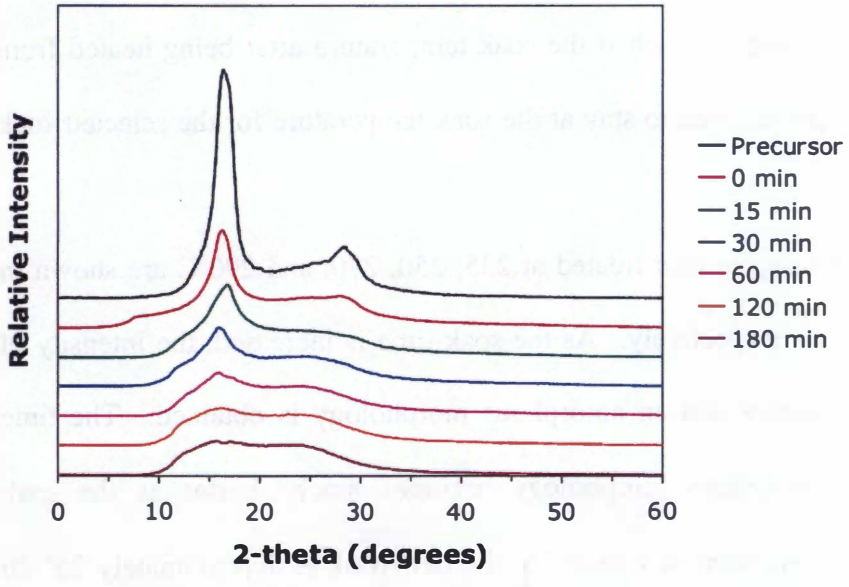

Figure 34. WAXS Scans for Samples Treated in Air at 250°C.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperature was 250°C and the soak times are indicated.

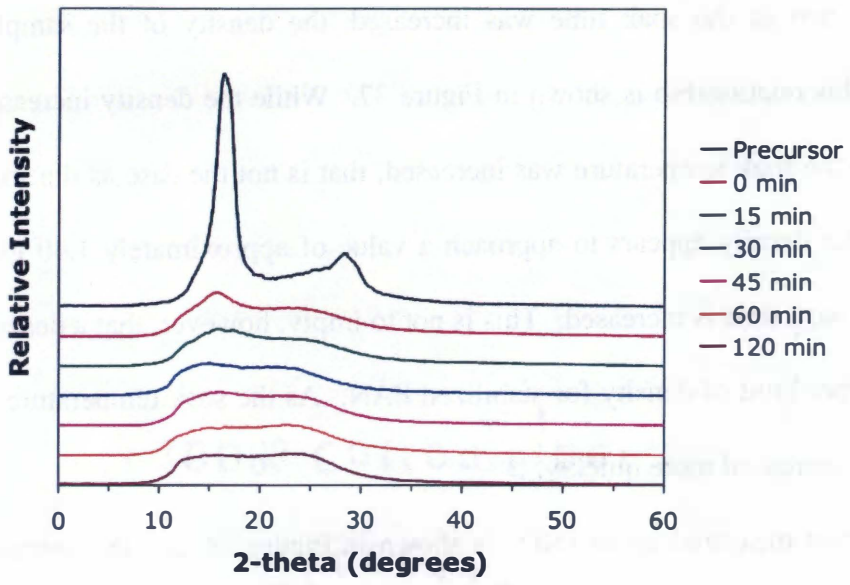

Figure 35. WAXS Scans for Samples Treated in Air at 270°C.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperature was 270°C and the soak times are indicated.

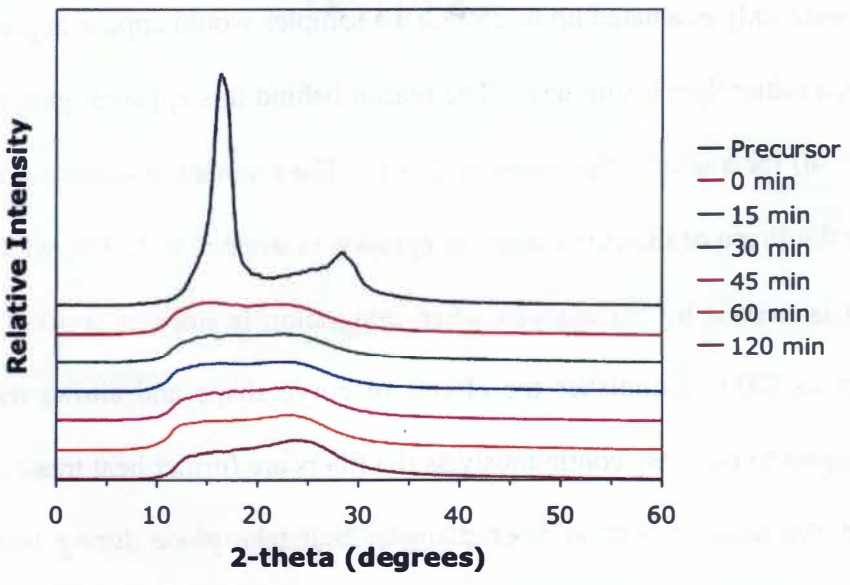

Figure 36. WAXS Scans for Samples Treated in Air at 290°C.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperature was 290°C and the soak times are indicated.

It was found that as the soak time was increased, the density of the samples increased as well. This relationship is shown in Figure 37. While the density increased in a linear fashion as the soak temperature was increased, that is not the case as the soak time is increased. The density appears to approach a value of approximately 1.40 g/cc asymptotically as the soak time is increased. This is not to imply, however, that a density of 1.40 g/cc is the upper limit of density for stabilized PAN. As the soak temperature is increased, the density increased more quickly.

The remnant heat measured up to 250°C is shown in Figure 38, and the remnant heat measured up to 300°C is shown in Figure 39. The shapes of the curves shown in both figures are essentially the same, with the remnant heat asymptotically approaching a value of 0 J/g as the soak time is increased. As seen in Table 4, however, it is noted that for the conventional precursor, ΔH_{250} was 77.94 J/g and ΔH_{300} was 1226.82 J/g. This means that if the data were only evaluated up to 250°C, the samples would appear to gain heat upon heat treatment rather than losing heat. The reason behind this apparent gain in heat is shown in Figure 40 for a soak temperature of 235°C. The remnant heat measured depends too greatly on the shape of the curve when integration is stopped at 250°C, while the majority of Peak I is studied by the analysis when integration is stopped at 300°C. Integrating the data up to 300°C diminishes the effects of curve shape and allows the remnant heat in the samples to decrease continuously as the fibers are further heat treated.

The changes in the ratio of core to fiber diameter that take place during heat treatment in air environment at atmospheric pressure are shown in Figure 41. As the soak

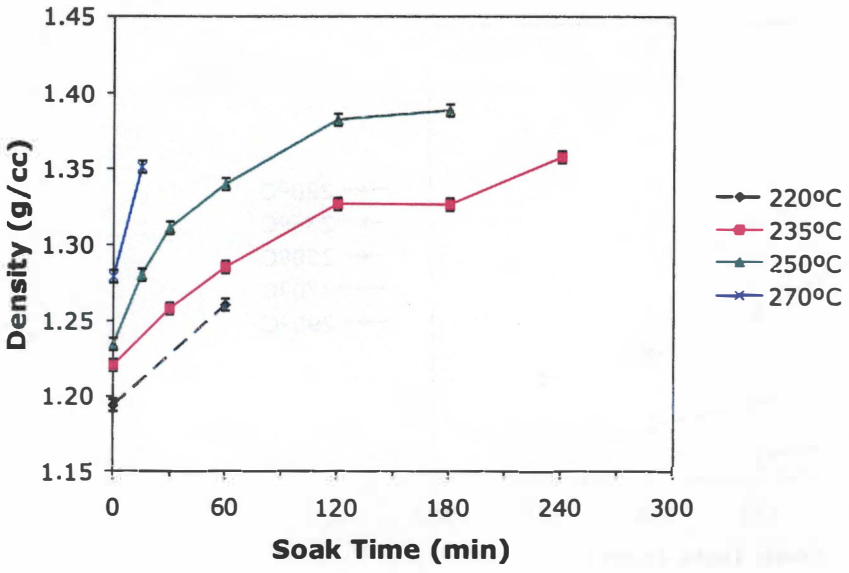

Figure 37. DGC Results for Samples Treated in Air.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperatures are indicated.

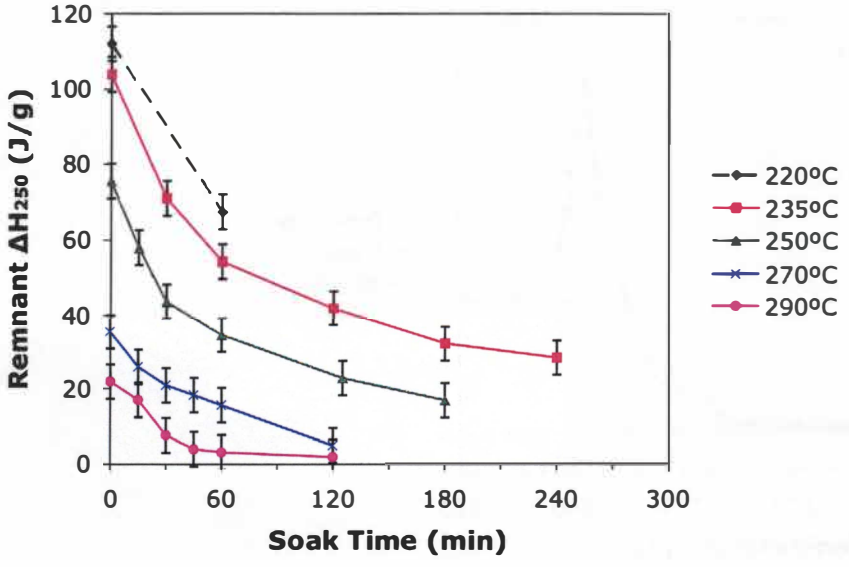

Figure 38. DSC Results for Samples Treated in Air and Integrated up to 250°C.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperatures are indicated.

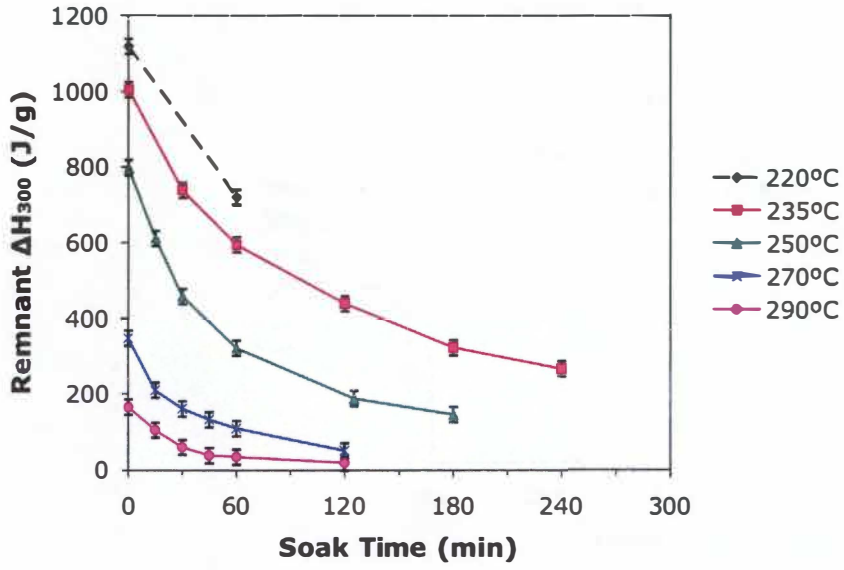

Figure 39. DSC Results for Samples Treated in Air and Integrated up to 300°C.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperatures are indicated.

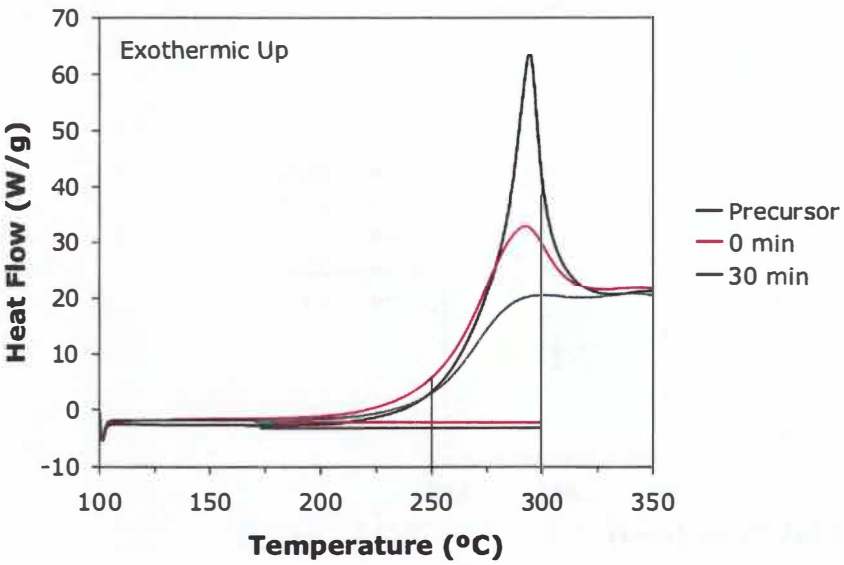

Figure 40. DSC Scans for Conventionally-Treated Samples.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperature was 235°C and the soak time is indicated.

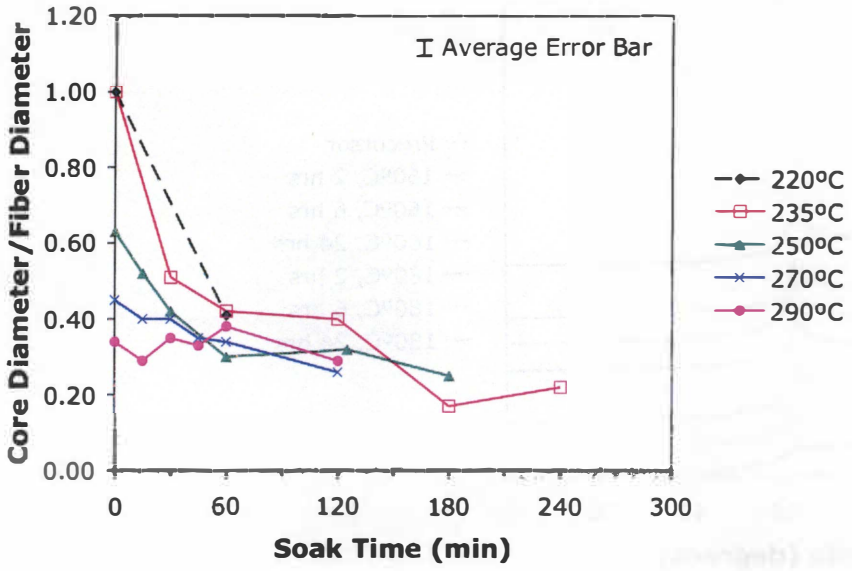

Figure 41. SEM Results for Samples Treated in Air.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperatures are indicated.

time is increased at a given soak temperature, the oxidized skin on the fiber surface grows thicker, causing the ratio of core diameter to fiber diameter to decrease. Even after 2 hours at 290°C, the core to fiber diameter ratio is still approximately 0.3, with very few samples having a core to fiber diameter less than 0.2. This observation led to the examination of samples with soak times up to 24 hours in order to determine the differences this extended amount of time would make and whether the samples would be fully oxidized after 24 hours.

Changes in WAXS scans for samples treated up to 24 hours at temperatures of 160 and 180°C are shown in Figure 42 and changes for samples treated at 250°C are shown in Figure 43. Based on the DSC scan for the conventional PAN precursor shown

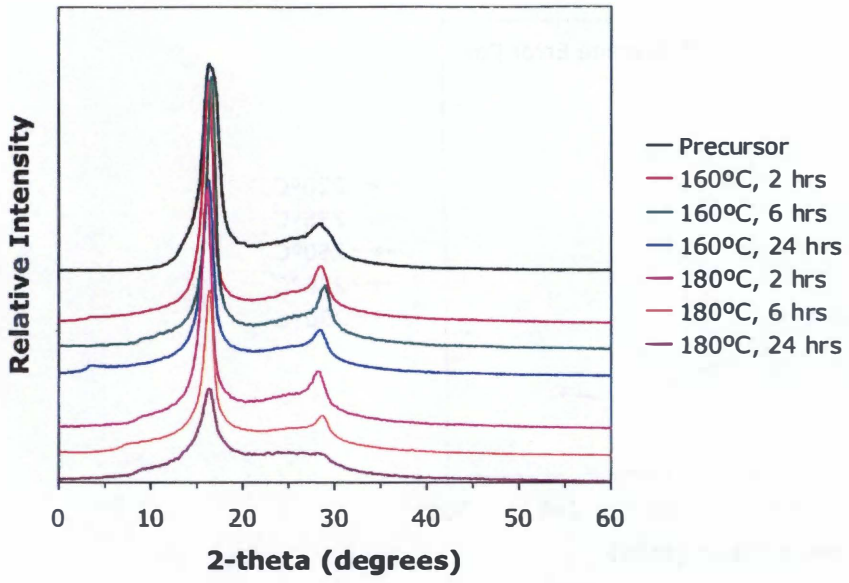

Figure 42. WAXS Scans for Treatment in Air at 160 and 180°C for up to 24 Hours.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperature was 160°C and the soak times are indicated.

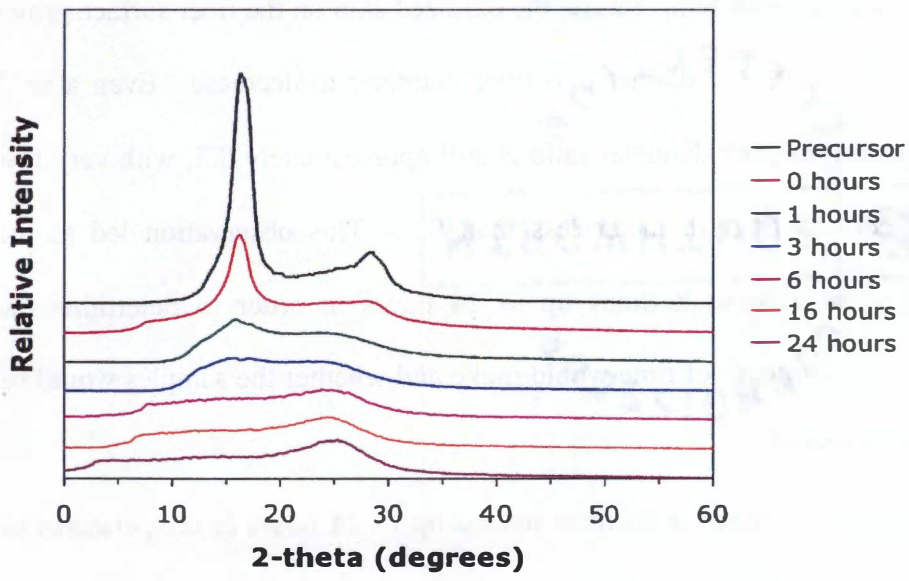

Figure 43. WAXS Scans for Samples Treated in Air at 250°C for up to 24 Hours.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperature was 250°C and the soak times are indicated.

in Figure 22, it is clear that 160 and 180°C are before the temperatures at which the major exothermic reactions take place. As such, it is expected that the precursor will not undergo major morphological changes at these temperatures, which is confirmed by Figures 42. Even after 24 hours soak time, the morphological structure of samples treated at 160 and 180°C is changed little from that of the original precursor except for the sharpening of the peak at 17° 2θ.

In contrast to samples heat treated at 160 and 180°C, samples treated at 250°C for up to 24 hours showed significant changes, as shown in Figure 43. After approximately 3 hours soak time at 250°C, the sample has an essentially amorphous structure. After 6 hours soak time, a new peak at approximately 25° 2θ appears and grows as the soak time is increased. The appearance of the peak at 25° 2θ highlights the importance of both temperature and time in the heat treatment of precursor fibers. At 250°C, it takes approximately 6 hours for the peak at 25° 2θ to appear, while at 290°C, it only takes 1 hour.

Changes in the remnant heat measured up to 300°C are shown in Figure 44 for samples heat treated up to 24 hours. Consistent with data from WAXS, samples heat treated at lower temperatures show modest change in the remnant heat. Samples treated at 250°C asymptotically approaches 0 J/g. It is interesting to note that once the sample begins to show signs of the new peak at 25° 2θ, the remnant heat of the samples is close to 0 J/g. This is true for samples treated at 250°C for 6 hours and samples treated at 290°C for 1 hour.

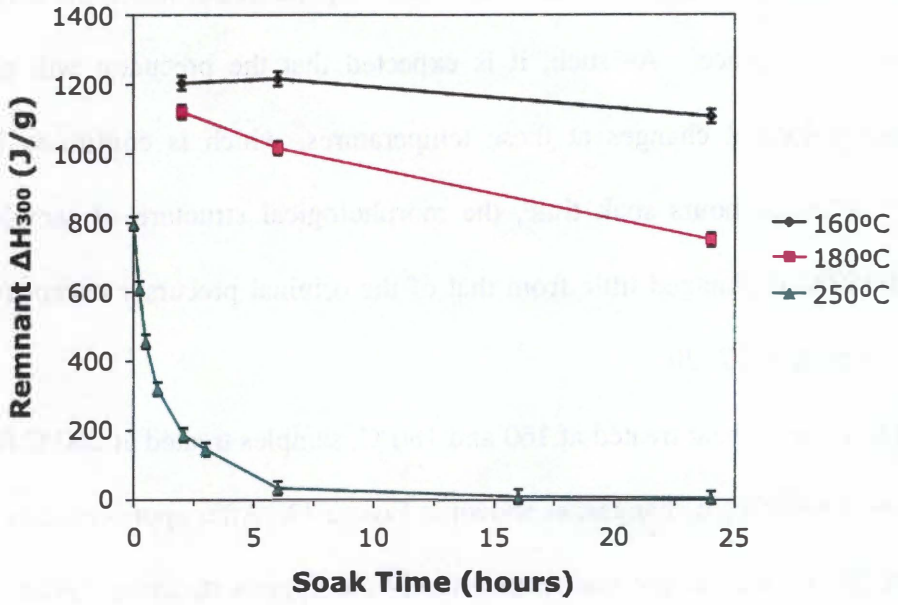

Figure 44. DSC Results for Samples Treated in Air for up to 24 Hours.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperatures are indicated.

Changes in the ratio of core to fiber diameter for samples treated up to 24 hours are shown in Figure 45. Samples heat treated at the lower temperatures (160, 180°C) showed no signs of a two-zone morphology and were eroded uniformly upon etching. For samples treated at 250°C, the diameter of the core region goes to 0 around 16 hours soak time. This means that the ratio of core to fiber diameter is 0 and that the fibers have been fully chemically oxidized.

From the data presented for treatment in air environment, it is clear that both temperature and time play an important role in the stabilization of PAN precursor. Although an attempt to determine the precise relationship between temperature and time

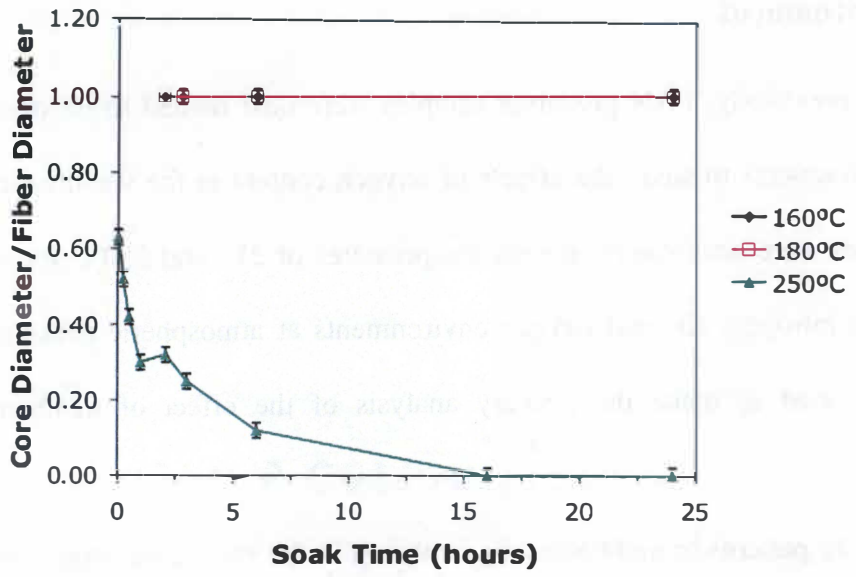

Figure 45. SEM Results for Samples Treated in Air for up to 24 Hours.

Precursor fiber samples were heat treated in air environment at atmospheric pressure. The soak temperatures are indicated.

was not made, general observations can be made. At temperatures of 220, 235, and 250°C for times of 1 hour soak time or less, it appears that an increase in temperature of 15°C results in fibers that are approximately equivalent to those treated at the lower temperature for times of 15 to 30 minutes soak time. This implies that an increase in temperature of 1°C at temperatures of 220 to 250°C is approximately equivalent to the addition of 1 to 2 minutes soak time during treatment at the lower temperature. At the higher soak temperatures of 270 and 290°C, an increase of 1°C appears to be approximately equivalent to the addition of 3 to 4 minutes soak time at the lower soak temperatures of 220 to 250°C.

5.2.3 Effect of Environment

As discussed previously, PAN precursor samples were heat treated in nitrogen, air, and oxygen environments to study the effects of oxygen content in the stabilization environment. Samples were heat treated at soak temperatures of 215 and 230°C for 60 minutes soak time in nitrogen, air, and oxygen environments at atmospheric pressure. These samples were used to make the primary analysis of the effect of treatment environment.

Changes in x-ray patterns brought about by treatment in the various environments are shown for samples treated at 215 and 230°C in Figure 46. At 215°C, samples treated in air environment have undergone more change than samples treated in nitrogen and oxygen environments. At 230°C, the differences between the samples treated in air and oxygen are less significant. Samples treated in nitrogen environment underwent the least change of the samples under consideration, independent of the soak temperature.

The changes in density that occur during heat treatment in these various environments are shown in Figure 47. As discussed previously, as the soak temperature is increased, the density increases as well. By conducting treatments in various environments, it is seen that the treatment environment plays an important role in the increase in density as well. Samples treated in nitrogen had lower densities than their counterparts treated in air and oxygen. For the samples treated in air and oxygen, the density was similar for samples treated at both soak temperatures.

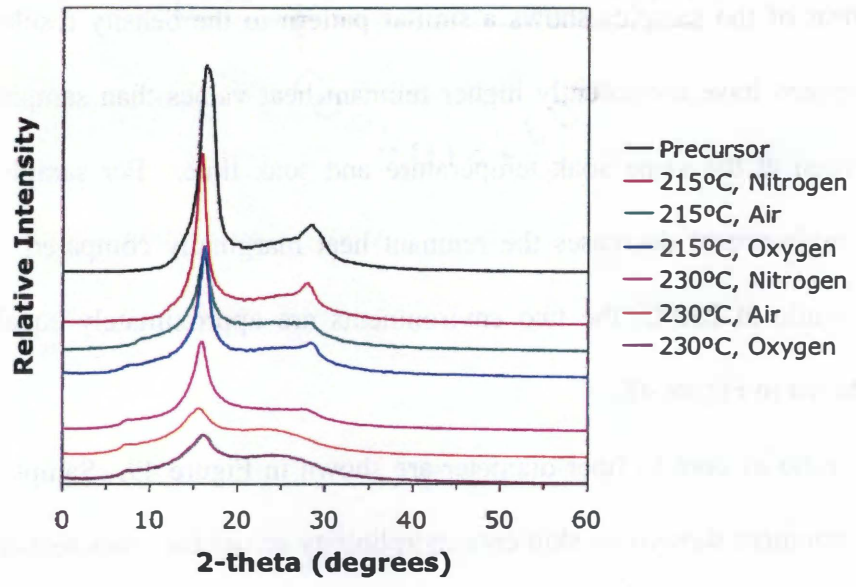

Figure 46. WAXS Scans for Treatment in Various Environments at 215 and 230°C.

Precursor fiber samples were treated at atmospheric pressure. The soak temperature was 215°C and the soak time was 60 minutes. The treatment environment is indicated.

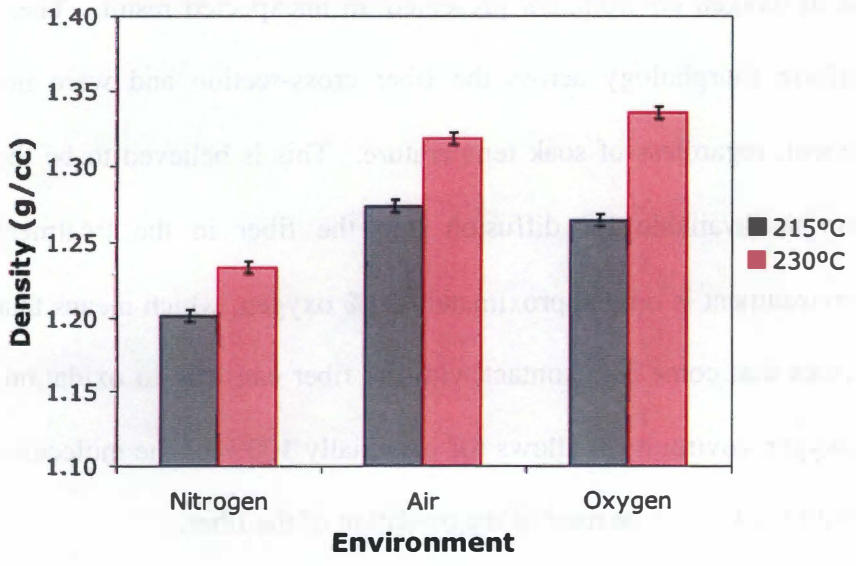

Figure 47. DGC Results for Samples Treated at 215 and 230°C.

Precursor fiber samples were heat treated at atmospheric pressure. The soak time was 60 minutes and the soak temperature and environment are indicated.

The remnant heat of the samples shows a similar pattern to the density results. Samples treated in nitrogen have consistently higher remnant heat values than samples treated in air and oxygen at the same soak temperature and soak time. For samples treated at 215°C, air environment decreases the remnant heat marginally compared to oxygen environment, while at 230°C, the two environments are approximately equal. The DSC results are shown in Figure 48.

Changes in the ratio of core to fiber diameter are shown in Figure 49. Samples treated in nitrogen environment showed no skin/core morphology across the cross-section of the fiber, and were eroded uniformly upon acid treatment. This was expected, as there was essentially no oxygen present in the treatment environment. Samples treated in air showed the expected decrease in core to fiber diameter ratio as the temperature was increased.

Samples treated in oxygen environment presented an unexpected result. These samples showed a uniform morphology across the fiber cross-section and were not eroded upon acid treatment, regardless of soak temperature. This is believed to be the result of the extra oxygen available for diffusion into the fiber in the treatment environment. An air environment is only approximately 20% oxygen, which means that only 20% of the molecules that come into contact with the fiber can lead to oxidation. On the other hand, an oxygen environment allows for essentially 100% of the molecules that come into contact with the fiber to be used in the oxidation of the fiber.

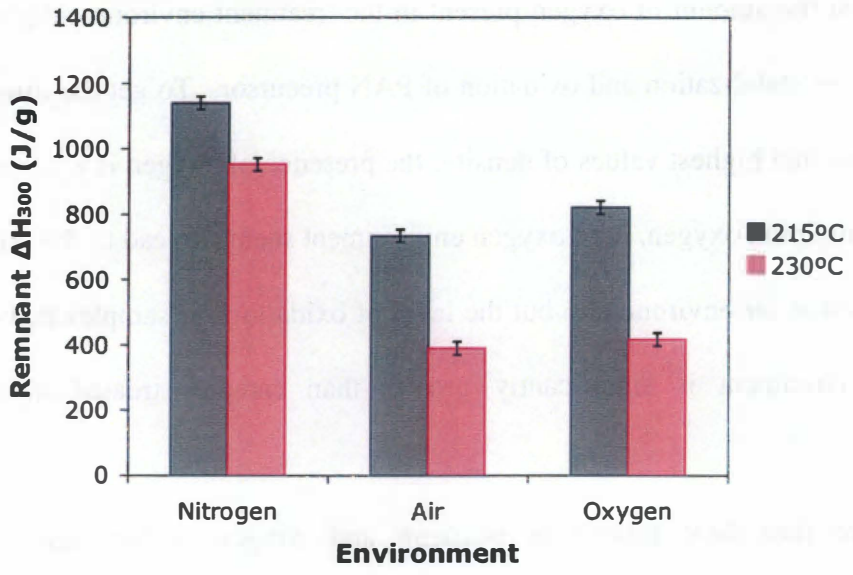

Figure 48. DSC Results for Samples Treated at 215 and 230°C.

Precursor fiber samples were heat treated at atmospheric pressure. The soak time was 60 minutes and the soak temperature and environment are indicated.

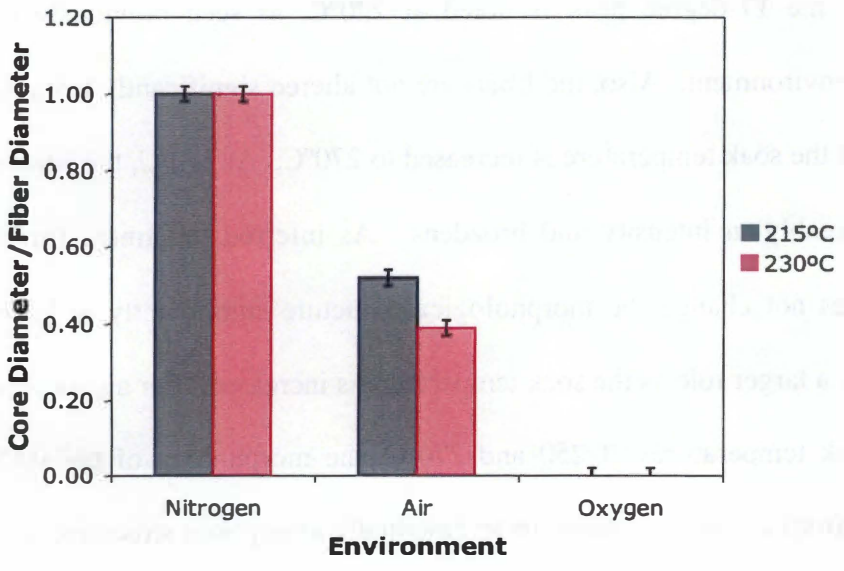

Figure 49. SEM Results for Samples Treated at 215 and 230°C.

Precursor fiber samples were heat treated at atmospheric pressure. The soak time was 60 minutes. The soak temperature and environment are indicated.

It appears that the amount of oxygen present in the treatment environment plays an important role in the stabilization and oxidation of PAN precursor. To get the lowest values of remnant heat and highest values of density, the presence of oxygen is essential. For environments containing oxygen, pure oxygen environment seems to lead to the same amount of stabilization as air environment, but the level of oxidation for samples treated in pure oxygen environment is significantly greater than samples treated in air environment.

Samples were then heat treated in nitrogen and oxygen environments at atmospheric pressure at soak temperatures and soak times similar to those already considered for treatment in air environment. The changes that occur in WAXS scans after treatment in nitrogen at various soak temperatures are shown in Figure 50. As shown, sharpening of the 17-degree peak is noted at 220°C, as seen previously for samples treated in air environment. Also, the fibers are not altered significantly from the original precursor until the soak temperature is increased to 270°C. At 270°C, the peak at 17° 2θ decreases noticeably in intensity and broadens. As inferred, treatment for 60 minutes soak time does not change the morphological structure significantly at lower temperatures, but plays a larger role as the soak temperature is increased. For a soak time of 60 minutes and soak temperatures of 250 and 270°C, the morphology of the PAN precursor is converted from a semi-crystalline to an essentially amorphous structure. It is also noted that there is no indication of a peak at 25° 2θ forming, as is the case for treatment in air environment at similar soak temperatures and soak times.

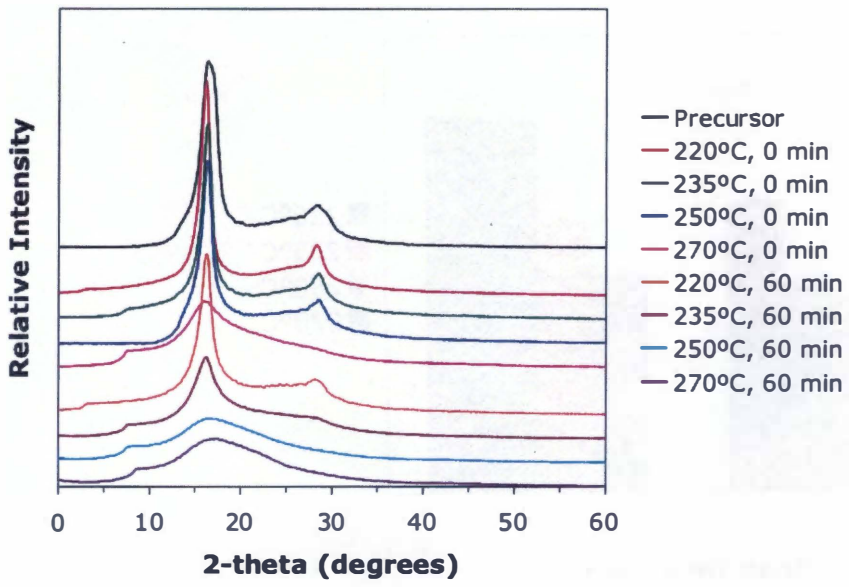

Figure 50. WAXS Scans of Samples Treated in Nitrogen.

Precursor fiber samples were heat treated in nitrogen environment at atmospheric pressure. The soak temperatures and soak times are indicated.

Density data for samples treated in nitrogen are shown in Figure 51. As shown for samples treated in air environment, density increases with both increases in soak temperature and soak time. Remnant heat values for samples treated in nitrogen also follow the trend established earlier for samples treated in air. As shown in Figure 52, as both soak temperature and soak time are increased, the remnant heat in the fibers is decreased.

The interesting result for all the samples treated in nitrogen is the drastic difference seen in samples treated at 270°C as compared to the other samples. The reason for this difference is shown in Figure 53. The PAN precursor used for the conventional

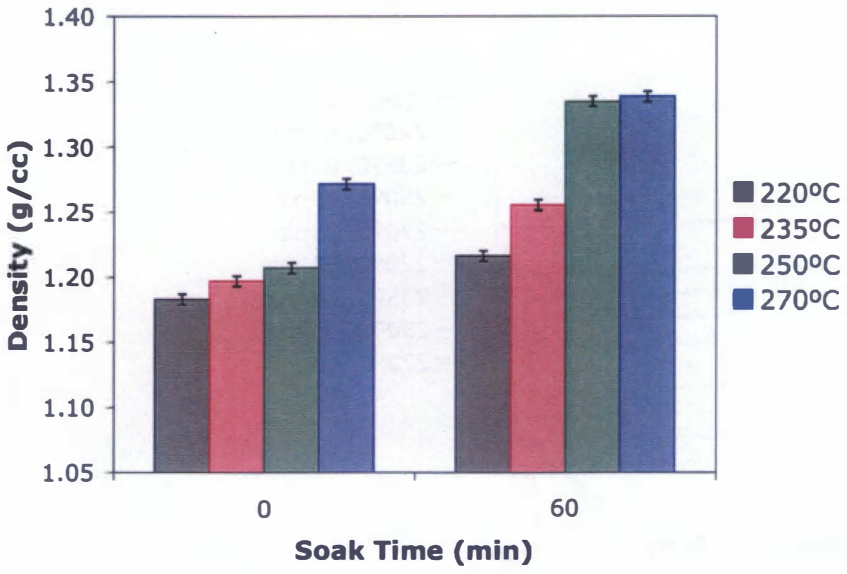

Figure 51. DGC Results for Samples Treated in Nitrogen.

Precursor fiber samples were heat treated in nitrogen environment at atmospheric pressure. The soak temperatures and soak times are indicated.

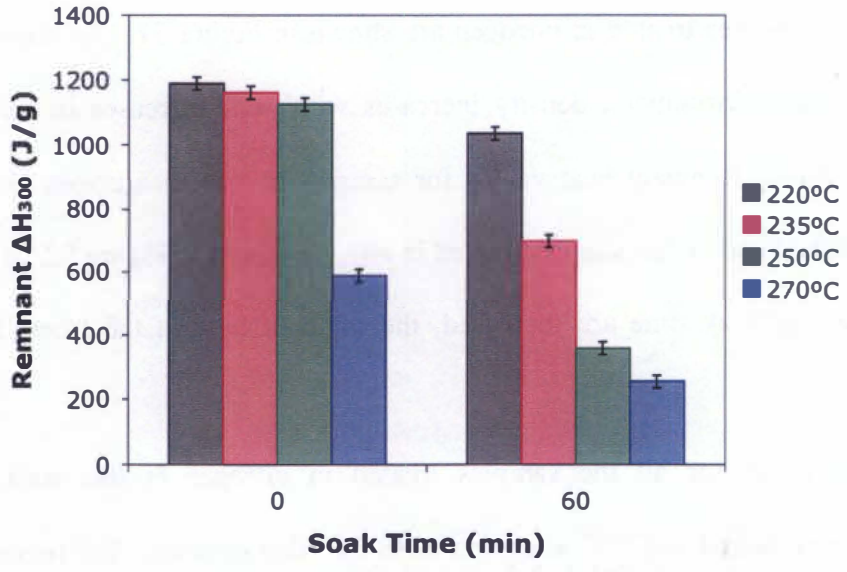

Figure 52. DSC Results for Samples Treated in Nitrogen.

Precursor fiber samples were heat treated in nitrogen environment at atmospheric pressure. The soak temperature and soak time are indicated.

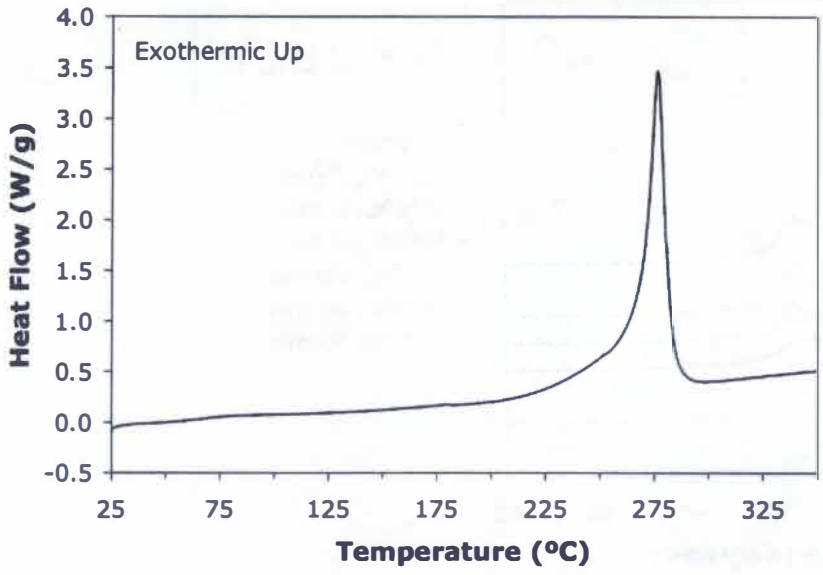

Figure 53. DSC Scan for Conventional PAN Precursor in Nitrogen Purge Gas.
The conventional PAN precursor was tested over the range of 25 to 350°C at a heat rate of 5°C/min. A nitrogen purge gas was used with a flow rate of 200 mL per minute.

heat treatments experiences a peak in the exothermic heat flow at approximately 275°C, which indicates that a major exothermic reaction is occurring in this temperature range. This is the reason for the larger change in morphological structure, higher density, and lower remnant heat.

Results are shown for samples treated in oxygen environment in Figures 54 through 56. Figure 54 details the changes that occur in the x-ray patterns upon heat treatment in oxygen environment. Increases in the density are shown in Figure 55 and the decreases in remnant heat are shown in Figure 56. The general features of these results are similar to the previously discussed cases of treatment in nitrogen and air. As

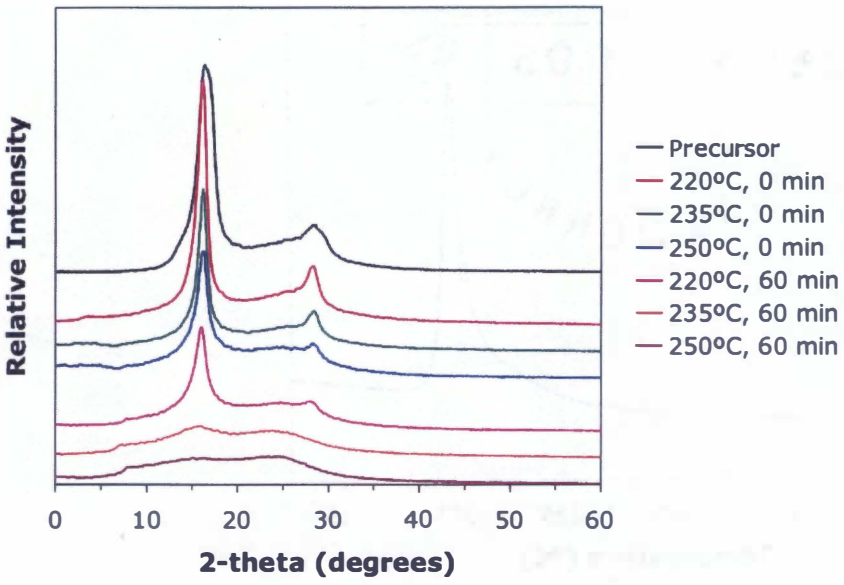

Figure 54. WAXS Scans of Samples Treated in Oxygen.

Precursor fiber samples were heat treated in oxygen environment at atmospheric pressure. The soak temperatures and soak times are indicated.

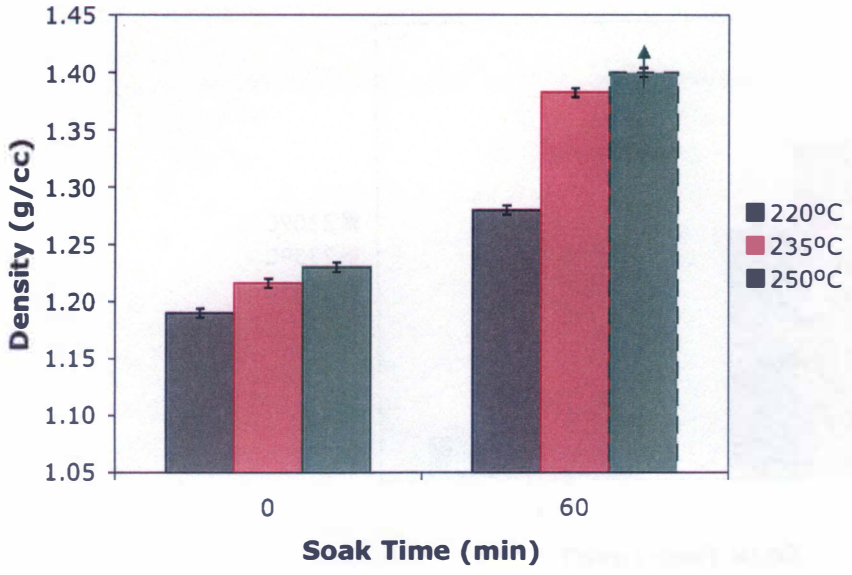

Figure 55. DGC Results for Samples Treated in Oxygen.

Precursor fiber samples were heat treated in oxygen environment at atmospheric pressure. The soak temperatures and soak times are indicated. Note: the sample treated at 250°C for 60 minutes had a density greater than 1.400 g/cc, and could not be measured by the range of the density gradient columns used.

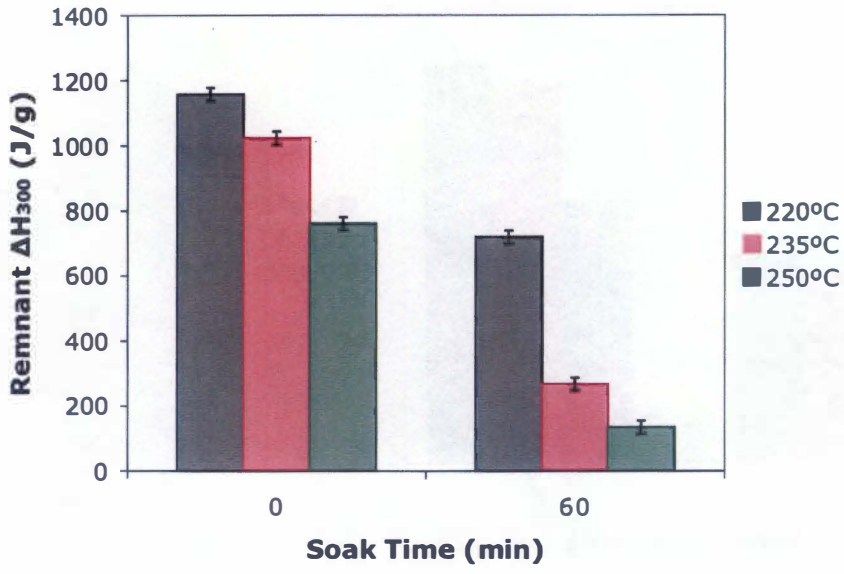

Figure 56. DSC Results for Samples Treated in Oxygen.

Precursor fiber samples were heat treated in oxygen environment at atmospheric pressure. The soak temperatures and soak times are indicated.

shown in all of these figures, as the soak temperature and soak time are increased, the samples progress further along in the stabilization process. Also, it is noted that samples treated in oxygen environment more closely resemble those treated in air environment, in that an emerging peak is noted around 25° 2θ, and one is not noted in samples treated in nitrogen environment.

Comparisons for the densities obtained in the various environments are given in Figures 57. Samples treated in nitrogen environment have lower densities than samples treated in air and oxygen environments, regardless of the soak temperature or soak time. In addition, samples treated in air and oxygen for 0 minutes soak time have densities that

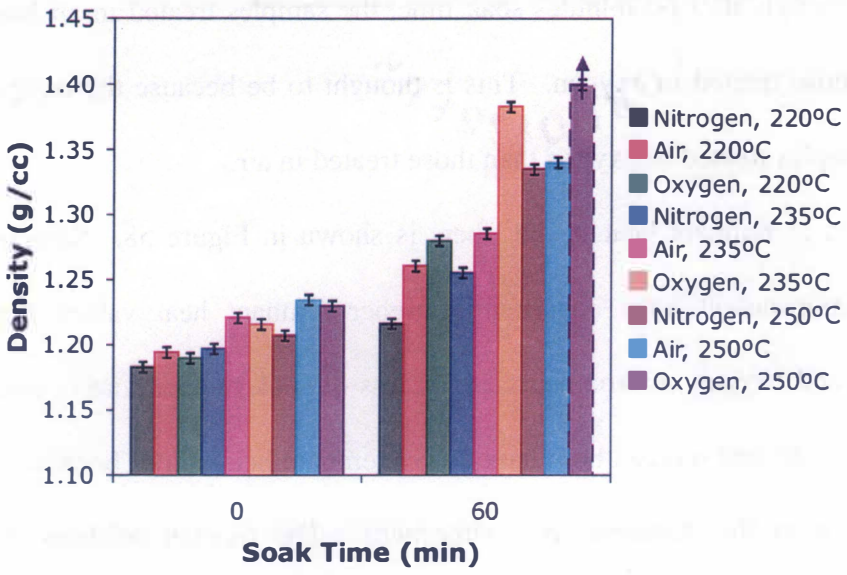

Figure 57. DGC Results for Samples Treated in Various Environments.

Precursor fiber samples were heat treated at atmospheric pressure. The soak temperature, soak time, and treatment environment are indicated. Note: the samples treated in oxygen environment at 250°C for 60 minutes had a density greater than 1.400 g/cc, and could not be measured by the range of the density gradient columns used.

are essentially equal, though after 60 minutes soak time, the samples treated in air have lower densities than those treated in oxygen. This is thought to be because the oxygen uptake is greater in samples treated in oxygen than those treated in air.

The comparison of remnant heat in the fibers is shown in Figure 58. Samples treated in nitrogen environment have consistently higher remnant heat values than samples treated in air and oxygen environments, regardless of soak temperature or soak time. Samples treated in air and oxygen both have lower remnant heat values because of the presence of oxygen in the stabilization environment. The oxygen oxidizes the samples while they undergo stabilization due to the treatment temperature, promoting cyclization and cross-linking reactions, which does not occur during treatment in inert environment. Dehydrogenation reactions are also reported to take place in oxidizing environment [29, 56], which would lower the remnant heat even further. For zero minutes soak time, all treatment environments produce samples with similar remnant heat values at low soak temperatures, but at higher soak temperatures the differences in inert and oxygen-containing environments become more pronounced. At 0 minutes soak time, remnant heat values for samples treated in both air and oxygen environments are similar.

At 60 minutes soak time, the differences in remnant heat values between samples treated in inert and oxygen-containing environments become more pronounced. For the oxygen-containing environments, at low soak temperatures, the remnant heat values are similar, but at higher soak temperatures, treatment in oxygen environment results in much lower values of remnant heat.

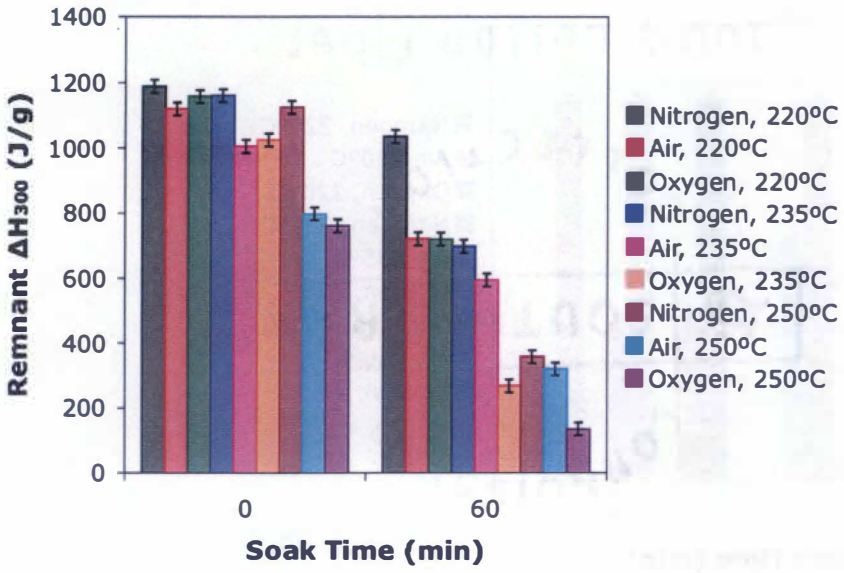

Figure 58. DSC Results for Samples Treated in Various Environments.
Precursor fiber samples were heat treated at atmospheric pressure. The soak temperature, soak time, and treatment environment are indicated.

Results of core and fiber diameter measurement are shown in Figure 59. As stated previously, samples treated in nitrogen did not undergo oxidation, and thus dissolved uniformly upon acid treatment. Samples treated in air showed a two-zone, or skin/core morphology across the cross-section, while samples treated in oxygen showed a uniformly oxidized morphology across the cross-section, regardless of soak temperature or soak time.

Love et al. [43] state that for samples they treated in air, the rate-limiting step is the formation of ladder polymer. Because of this, oxygen in the treatment environment has sufficient time to diffuse into the fiber and oxidize all of the ladder polymer as it

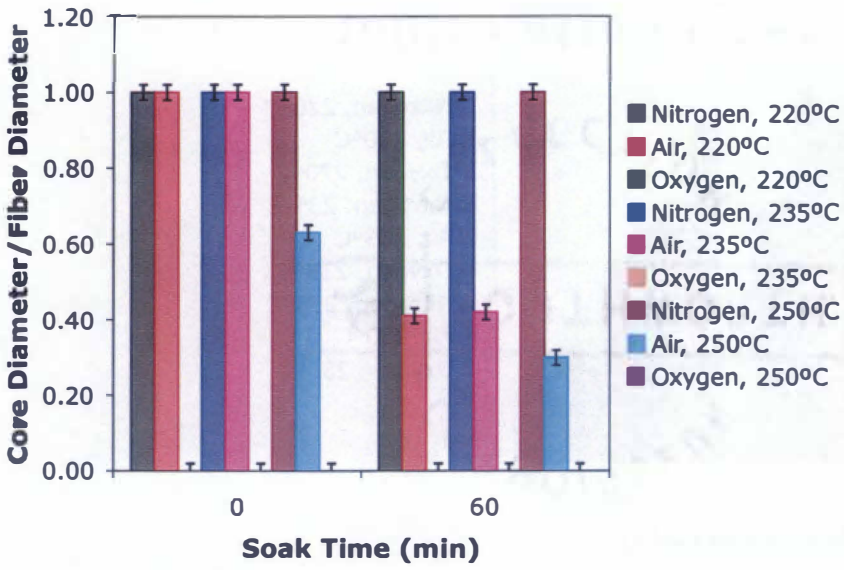

Figure 59. SEM Results for Samples Treated in Various Environments.

Precursor fiber samples were heat treated at atmospheric pressure. The soak temperature, soak time, and treatment environment are indicated. Note: samples treated in oxygen environment showed a uniform morphology across the cross-section and were not eroded upon acid treatment.

forms, resulting in a uniform morphology across the cross-section. For samples treated in vacuum prior to air, the rate limiting step was the diffusion of oxygen, which led to the formation of a skin/core morphology across the cross-section.

While it is debatable whether the heat treatments given to the precursor material under consideration are the sole reason behind Love et al.'s results, the finding that the rate limiting step is the formation of ladder polymer is an important one, which explains the differences between treatment in air and oxygen environments. As stated previously, air environment contains only about 20% oxygen, so only about 20% of the gas molecules coming into contact with the fiber during heat treatment can lead to oxidation. On the other hand, the oxygen environment was essentially 100% oxygen, which means that approximately 100% of the gas molecules coming into contact with the fiber can lead to oxidation. Once the ladder polymer forms, oxygen is in abundant supply to participate in oxidation and cross-linking reactions throughout the entire fiber in samples treated in oxygen environment, which leads to a more amorphous structure, higher densities, and lower remnant heat values at higher soak temperatures and soak times. At lower soak temperatures and soak times, the air and oxygen environments both yielded samples that were similar in crystalline structure, density, and remnant heat.

In summary, the presence of oxygen in the treatment environment promotes the formation of an amorphous structure, higher density, and lower remnant heat values at lower soak temperatures and soak times than would be necessary in inert environments. For oxidizing environments, the presence of excess oxygen promotes these changes in a similar manner for shorter soak times and in a greater manner for longer soak times, for a

given soak temperature. Treatment in oxygen environment also leads to the formation of fully oxidized fibers with uniform fiber cross-sections, whereas treatment in air environment leads to the formation of a skin/core morphology across the fiber cross-section. However, it is debatable whether the presence of excess oxygen in the treatment environment improves stabilization. This is due to the unclear effects that these factors would have on the final carbon fibers. This statement is supported in part by the research of Grove and Abhiraman [56], who found that if oxygen is added in excess, the zones of high oxygen concentration may lead to excessive cleavage when exposed to the high temperatures of carbonization.

5.2.4 Effect of Pressure

In order to study the effect of pressure during the stabilization of PAN, precursor samples were heat treated in air environment at a soak temperature of 230°C for a soak time of 60 minutes. The pressure was varied from a partial vacuum of 0.5 atmospheres up to 5 atmospheres absolute pressure.

X-ray scattering patterns are shown in Figure 60. Changes in treatment pressure appear to have no major effect on the morphology of the fiber samples as measured by x-ray scattering. Based on WAXS data, all samples appear to be at approximately the same point in the stabilization process. The densities of the samples, as seen in Figure 61, show a different result. The density of the fiber samples is nearly linearly proportional to

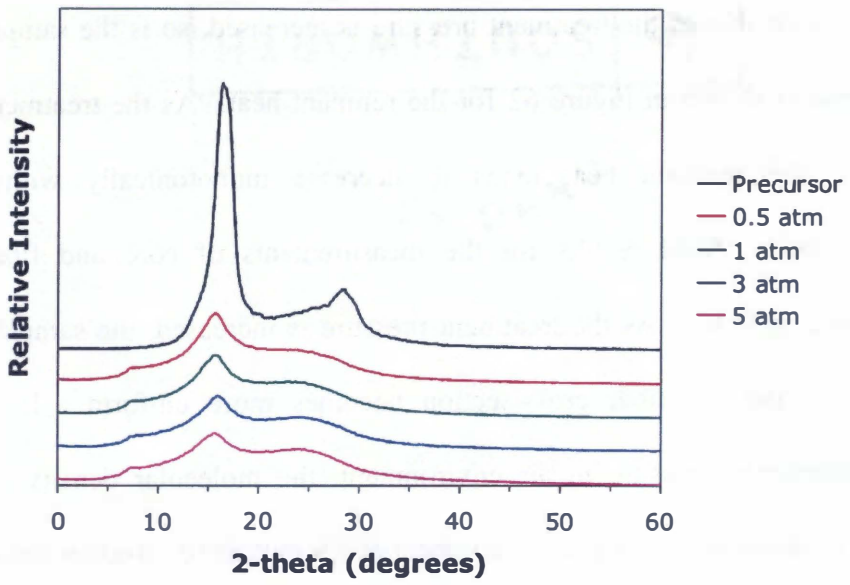

Figure 60. WAXS Scans for Samples Treated at 230°C at Various Pressures.

Precursor fiber samples were heat treated in air environment. The soak temperature was 230°C and the soak time was 60 minutes. The pressure is indicated.

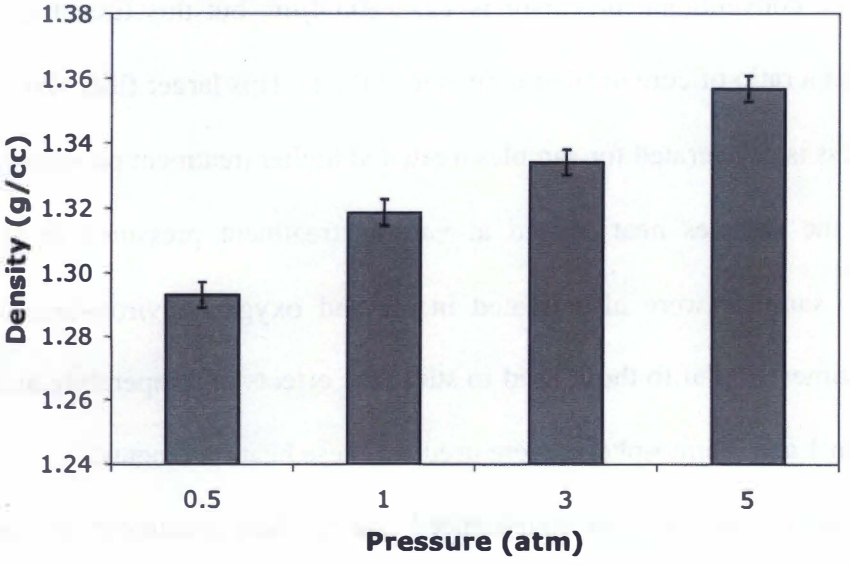

Figure 61. DGC Results for Samples Treated at 230°C at Various Pressures.

Precursor fiber samples were heat treated in air environment. The soak temperature was 230°C and the soak time was 60 minutes. The treatment pressure is indicated.

the treatment pressure, such that as the treatment pressure is increased, so is the sample density. A similar trend is shown in Figure 62 for the remnant heat. As the treatment pressure is increased, the remnant heat tends to decrease monotonically within experimental error. Finally, SEM results for the measurements of core and fiber diameters are shown in Figure 63. As the treatment pressure is increased, the samples undergo more oxidation and the fiber cross-section becomes more uniform. It is interesting that 5 atmospheres pressure in air environment, the molecular density of oxygen is approximately the same as oxygen environment at 1 atmosphere. Both of these treatment conditions gives a uniform cross-section across the fiber diameter.

Micrographs for the sample treated for 60 minutes at 230°C at 3 atmospheres pressure in air environment can be seen in Figure 64. The large majority of fibers examined in this sample had a uniform cross-section, but one larger fiber did not. The average diameter for the conventional precursor is 12.72±0.64μm, but this fiber had a diameter of 16.8 μm and a ratio of core to fiber diameter of 0.24. This larger fiber shows that the oxidation process is accelerated for samples treated at higher treatment pressures.

In addition to the samples heat treated at various treatment pressures in air environment at 230°C, samples were also treated in air and oxygen environment at temperatures and soak times similar to those used to study the effects of temperature and time. Pressures between 1 and 3 atmospheres were used for these heat treatments.

The morphological changes the samples experienced during heat treatment in air environment can be judged from Figures 65, 66, and 67 for soak temperatures of 220,

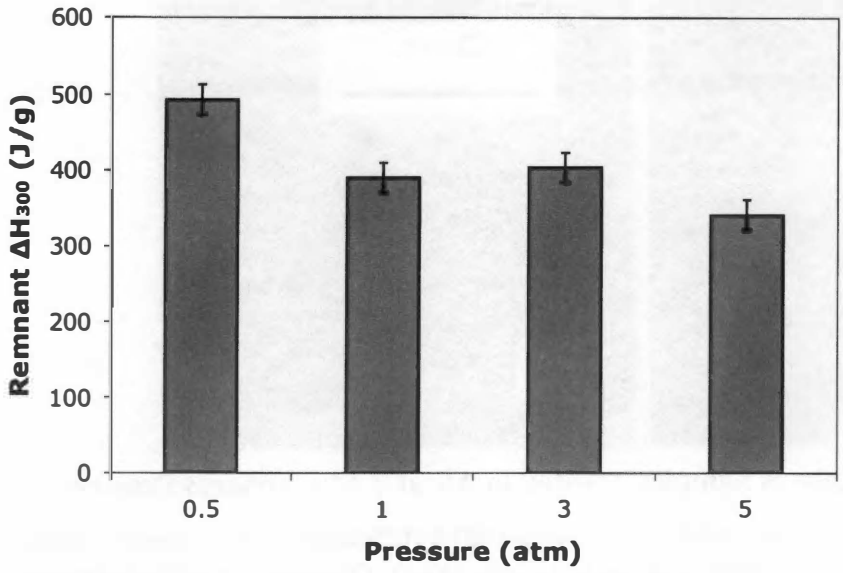

Figure 62. DSC Results for Samples Treated at 230°C at Various Pressures.

Precursor fiber samples were heat treated in air environment. The soak temperature was 230°C and the soak time was 60 minutes. The treatment pressure is indicated.

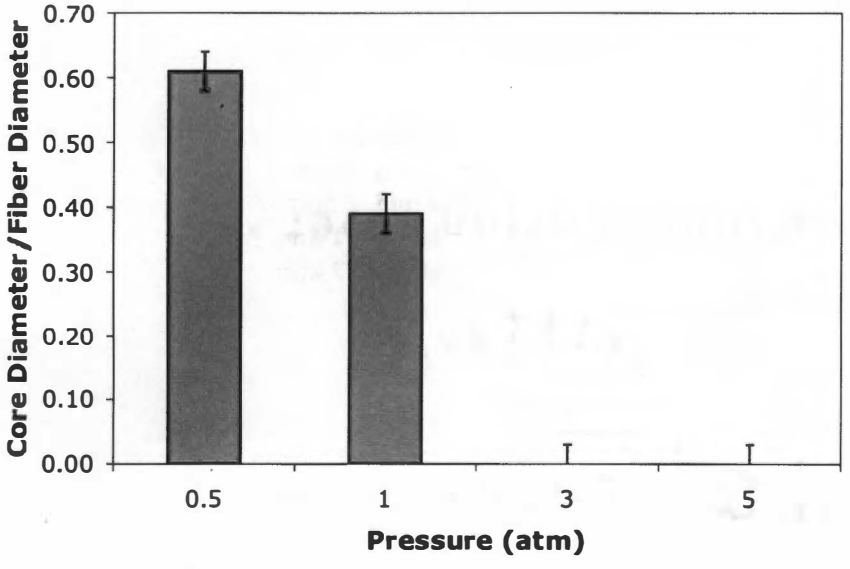

Figure 63. SEM Results for Samples Treated at 230°C at Various Pressures.

Precursor fiber samples were heat treated in air environment. The soak temperature was 230°C and the soak time was 60 minutes. The treatment pressure is indicated.

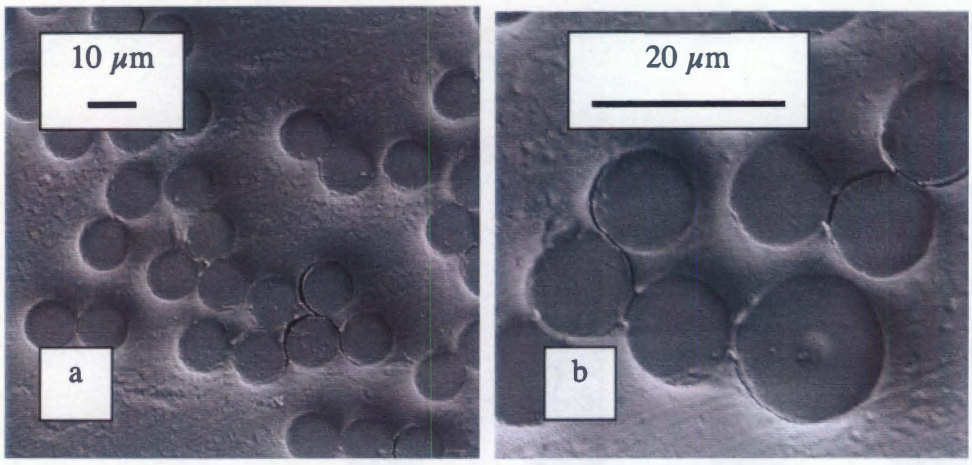

Figure 64. Micrographs of Samples Treated in Air at 3 Atmospheres Pressure.

Precursor fiber samples were heat treated in air environment at 3 atmospheres pressure. The soak temperature was 230°C and the soak time was 60 minutes. Fibers in (a) show a uniform cross-section, while the fiber in (b) is a larger diameter outlier showing a skin/core morphology. The outlier had a diameter of 16.8 μm and a core to fiber diameter ratio of 0.24.

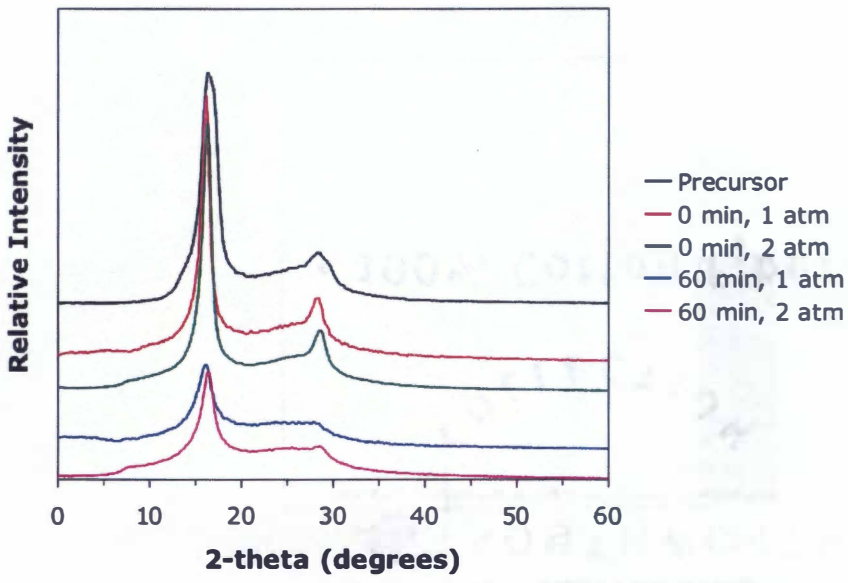

Figure 65. WAXS Scans for Samples Treated in Air at Various Pressures at 220°C.

Precursor fiber samples were heat treated in air environment. The soak temperature was 220°C. The soak time and treatment pressure are indicated.

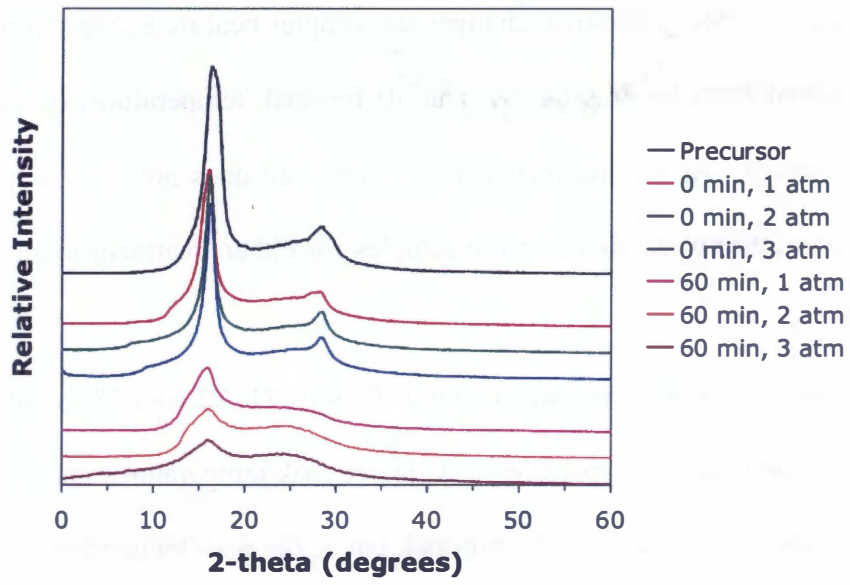

Figure 66. WAXS Scans for Samples Treated in Air at Various Pressures at 235°C.

Precursor fiber samples were heat treated in air environment. The soak temperature was 235°C. The soak times and treatment pressures are indicated.

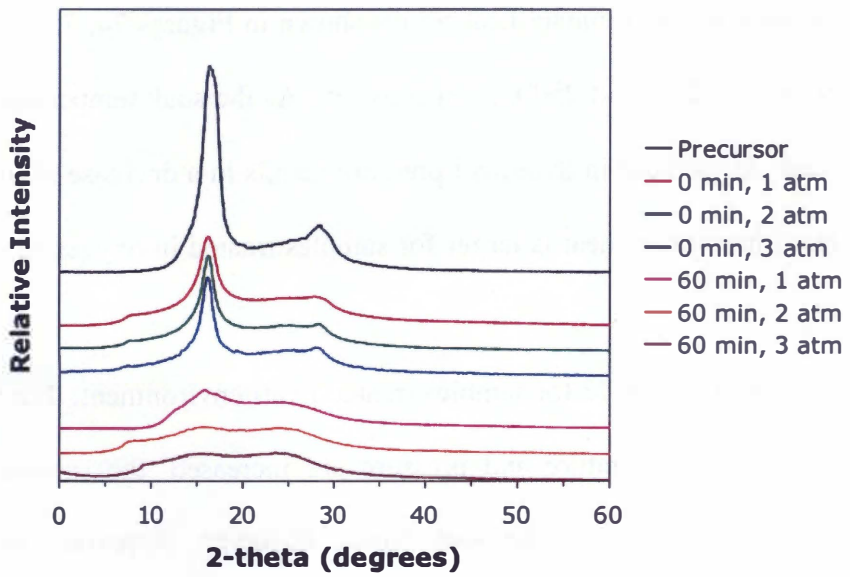

Figure 67. WAXS Scans for Samples Treated in Air at Various Pressures at 250°C.

Precursor fiber samples were heat treated in air environment. The soak temperature was 250°C. The soak times and treatment pressures are indicated.

235, and 250°C, respectively. Morphological changes for samples heat treated in oxygen environment can be judged from Figures 68, 69, and 70 for soak temperatures of 220, 235, and 250°C, respectively. As before, increasing the pressure does not bring about major changes in the crystallinity remaining in the samples for either treatment in air or oxygen environments.

Results from density measurements are shown in Figures 71, 72, and 73 for soak temperatures of 220, 235, and 250°C, respectively. At lower soak temperatures and soak times, the effects of pressure on the density are minimal, but as the soak temperature and soak time are increased, treatment pressure is an important factor in the density obtained during heat treatment. The effects of treatment pressure are greater for samples treated in oxygen environment than in air environment; samples treated in oxygen have higher densities than samples treated in air after 60 minutes soak time.

Similar results are seen for the remnant heat results shown in Figures 74, 75, and 76 for soak temperatures of 220, 235, and 250°C, respectively. As the soak temperature and soak time are increased, an increase in treatment pressure results in a decrease in the remnant heat. The decrease in remnant heat is larger for samples treated in oxygen than air environment.

SEM results are shown in Figure 77 for samples treated in air environment. For 0 minute soak times, as the soak temperature and pressure are increased, the samples become more fully oxidized. For 60 minute soak times, however, increasing the treatment pressure to 2 atmospheres seems to create a larger barrier to oxidation in the

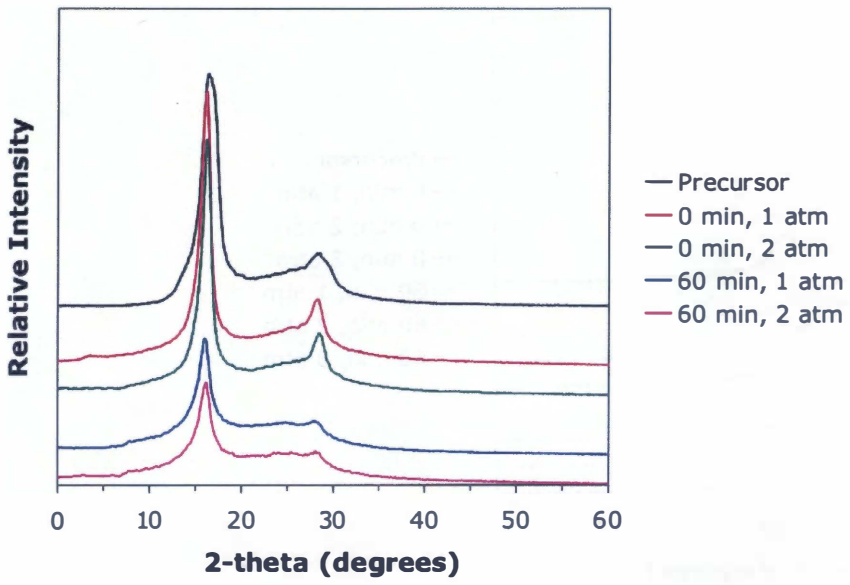

Figure 68. WAXS Scans for Treatment in Oxygen at Various Pressures at 220°C.

Precursor fiber samples were heat treated in oxygen environment. The soak temperature was 220°C. The soak time and treatment pressure are indicated.

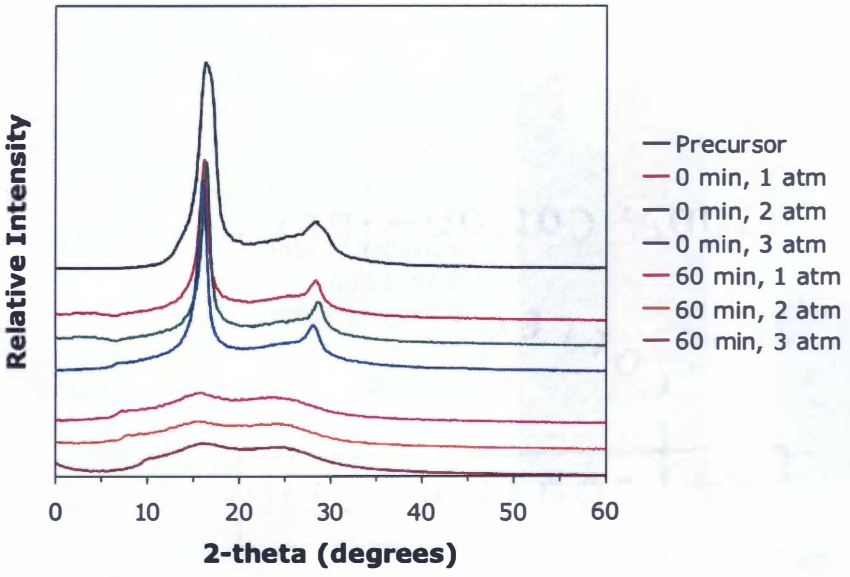

Figure 69. WAXS Scans for Treatment in Oxygen at Various Pressures at 235°C.

Precursor fiber samples were heat treated in oxygen environment. The soak temperature was 235°C. The soak times and treatment atmospheres are indicated.

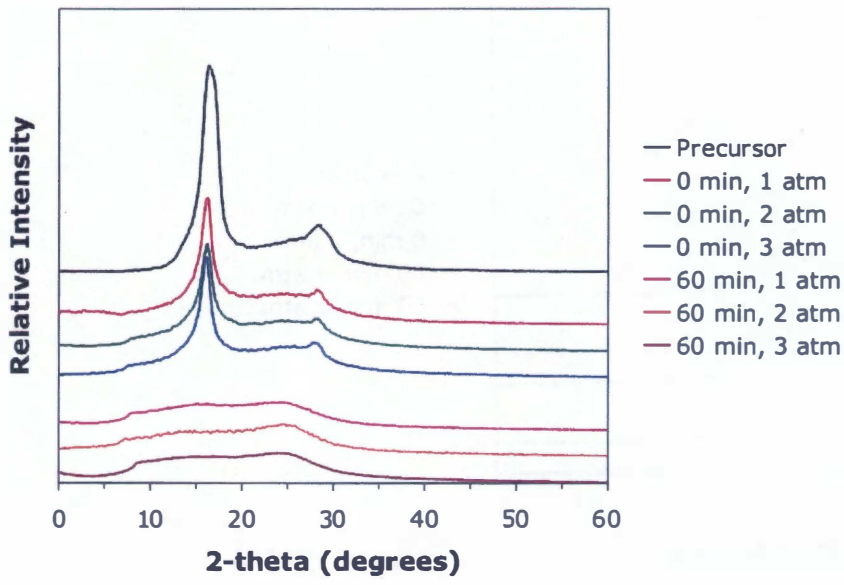

Figure 70. WAXS Scans for Treatment in Oxygen at Various Pressures at 250°C.

Precursor fiber samples were heat treated in oxygen environment. The soak temperature was 250°C. The soak times and treatment pressures are indicated.

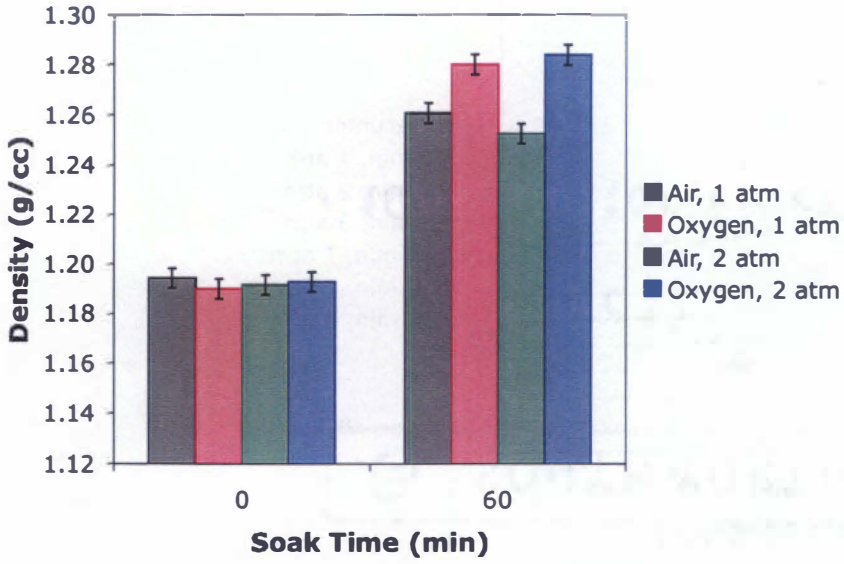

Figure 71. DGC Results for Samples Treated at 220°C at Various Pressures.

Precursor fiber samples were heat treated at a soak temperature of 220°C. The environment, pressure, and soak time are indicated.

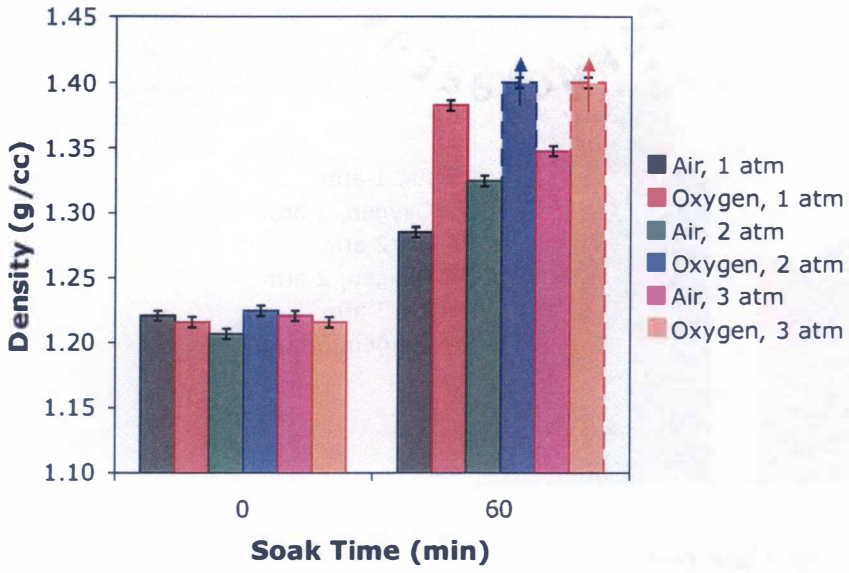

Figure 72. DGC Results for Samples Treated at 235°C at Various Pressures.

Precursor fiber samples were heat treated at a soak temperature of 235°C. The environment, pressure, and soak time are indicated. Samples treated in oxygen environment at pressures of 2 and 3 atmospheres for 60 minutes soak time had densities greater than 1.400 g/cc and could not be measured.

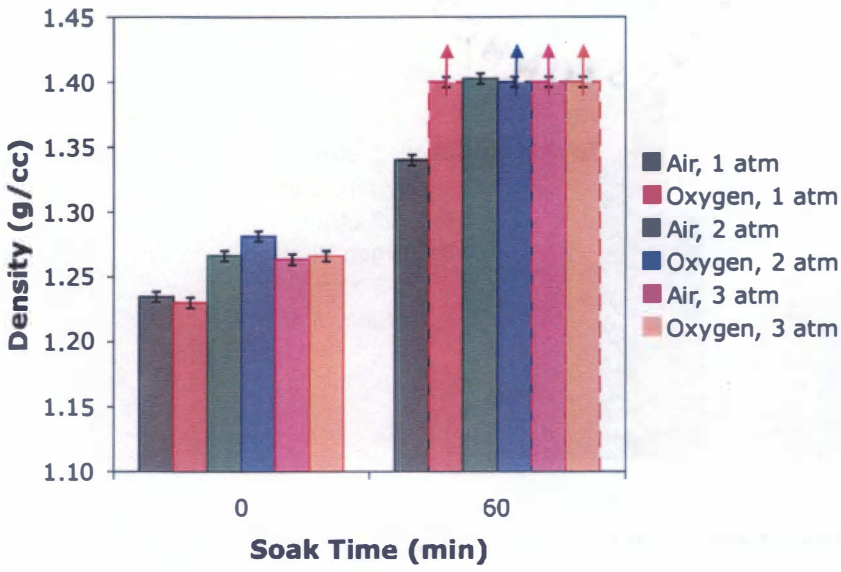

Figure 73. DGC Results for Samples Treated at 250°C at Various Pressures.

Precursor fiber samples were heat treated at a soak temperature of 250°C. The environment, pressure, and soak time are indicated. Samples treated in air environment at a pressure of 3 atmospheres for 60 minutes soak time and samples treated in oxygen environment for 60 minutes soak time had densities greater than 1.400 g/cc and could not be measured.

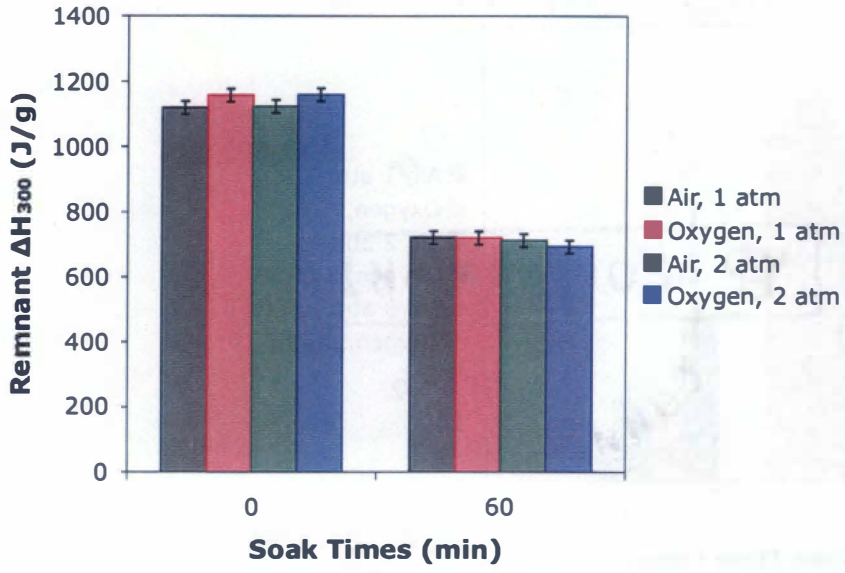

Figure 74. DSC Results for Samples Treated at 220°C at Various Pressures.

Precursor fiber samples were heat treated at a soak temperature of 220°C. The environment, pressure, and soak time are indicated.

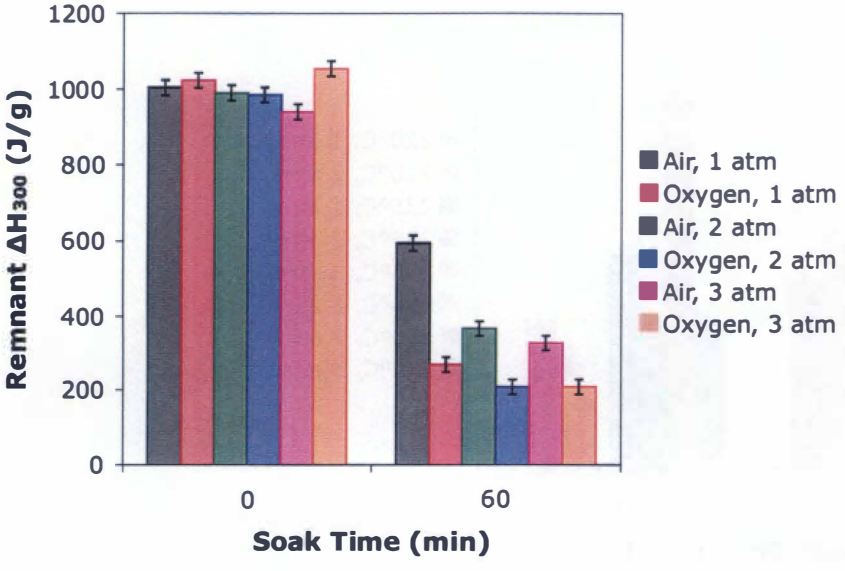

Figure 75. DSC Results for Samples Treated at 235°C at Various Pressures.

Precursor fiber samples were heat treated at a soak temperature of 235°C. The environment, pressure, and soak time are indicated.

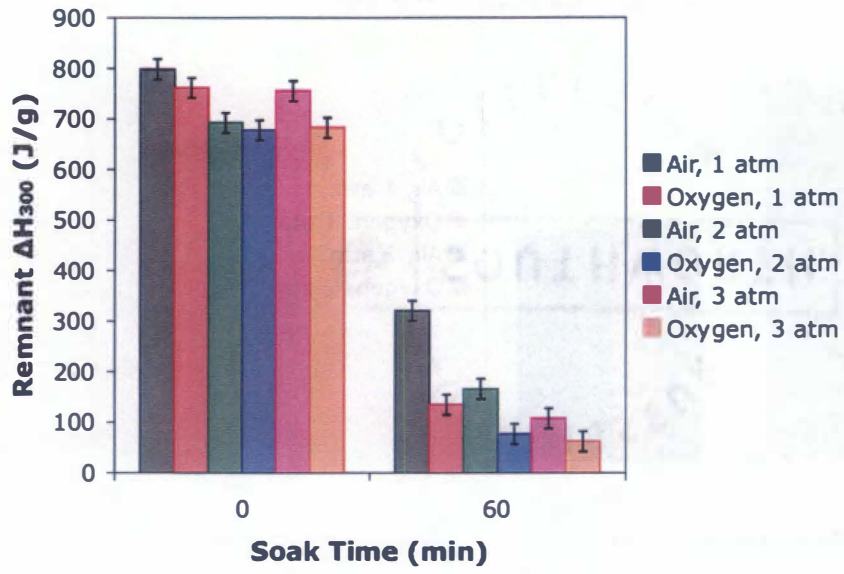

Figure 76. DSC Results for Samples Treated at 250°C at Various Pressures.

Precursor fiber samples were heat treated at a soak temperature of 250°C. The environment, pressure, and soak time are indicated.

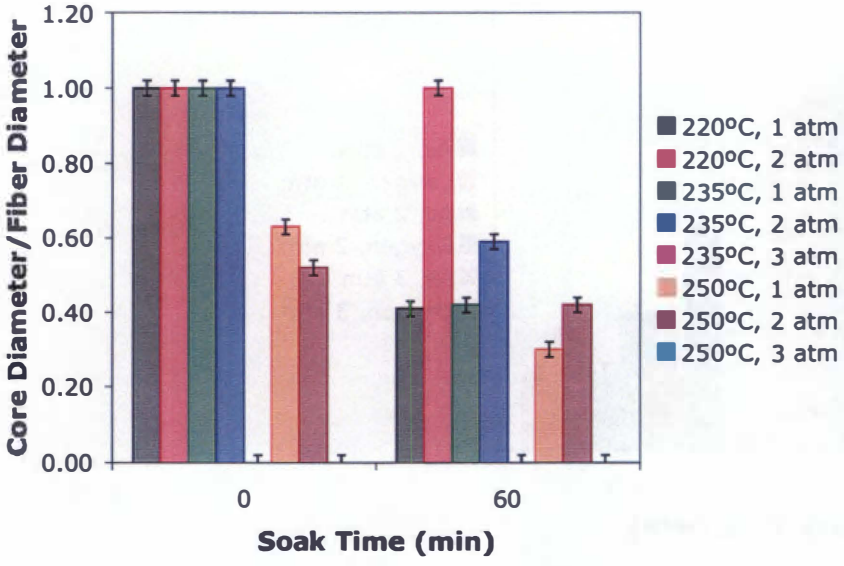

Figure 77. SEM Results for Samples Treated in Air at Various Pressures.

Precursor fiber samples were heat treated in air environment. The pressure, soak temperature, and soak time are indicated.

fiber, as shown by the higher core to fiber diameter ratios for all samples treated at 2 atmospheres pressure. When the treatment pressure is further increased to 3 atmospheres, the fibers become fully oxidized. Increasing the treatment pressure for samples treated in oxygen environment had no measurable effect; samples treated in oxygen, regardless of the treatment pressure, showed a uniform morphology across the fiber cross-section.

In summary, increasing the treatment pressure has little effect on the rate of stabilization reactions at soak times of 0 minutes, regardless of temperature. For soak times of 60 minutes, the rate of stabilization increases as the treatment pressure is increased. Increasing the pressure to 2 atmospheres in air environment has a retardation effect on the oxidation of the fibers, but this effect is overcome when the pressure is increased to 3 atmospheres.

5.3 Progression of Stabilization

Although the testing performed on the stabilized PAN fibers does not detail the specific chemical reactions that occur during the stabilization process, the testing results do lend insight into the process.

It is first interesting to note that when the formation of a skin/core morphology is first observed in both the commercial and conventionally-treated samples, the thickness of the skin layer accounts for approximately 40 to 50% of the fiber radius, as shown in Figures 27, 41, 49, 59, 63, and 77. Warner et al. [28] noted similar results, stating that when the skin layer was first observed in fibers undergoing diffusion-limited reactions,

the skin layer already occupied approximately 40 to 50% of the radius. The reasons behind this result are unclear, but it appears that after a certain level of stabilization is reached, a change in the progression of stabilization occurs, causing a barrier to the diffusion of oxygen to occur, which results in the formation of the skin/core morphology.

Warner et al. [28] addressed this finding by dividing the stabilization process into two stages. In the first stage of stabilization, "prefatory" reactions take place. Prefatory reactions are defined as those reactions involved in the initiation and polymerization of nitrile groups. Oxidative reactions may be involved in this stage of stabilization, acting to generate hydroperoxides, carboxylates, and other active groups that initiate nitrile polymerization. If the second stage of stabilization reactions does not occur simultaneously, the fiber produced at the end of the prefatory reactions will be reddish-brown, will be etched by sulfuric acid, and will burn when exposed to the flame of a match.

In the second stage of stabilization, "sequent" reactions take place. These reactions occur when the products of prefatory reactions are exposed to oxygen. The reddish-brown color changes rapidly to black, and this black material will not be etched by sulfuric acid. In addition, it will not burn when exposed to the flame of a match. It should be noted that these two stages were used to describe the process of stabilization, and no detail was given concerning the underlying chemistry. These results were also found to be dependent on factors such as temperature, fiber size, and fiber chemistry [28].

It is also interesting to note the differences between treatments in inert and oxygen-containing environments. Treatment in inert environment resulted in fibers with

lower densities and higher values of remnant heat. In an inert environment, the only reactions taking place are prefatory reactions, or more generally, cyclization reactions.

This is not the case in an oxidizing environment, however. In addition to cyclization reactions, which are promoted in oxidizing environment, there are dehydrogenation, oxidation, and cross-linking reactions, all of which are occurring at essentially the same time. The absorption of oxygen accounts for the higher densities obtained, and the acceleration of cyclization and addition of other reactions explains why the remnant heat for these samples is lower.

With this knowledge, it is possible to propose a possible progression for the thermo-oxidative stabilization of PAN precursor. Once sufficient temperature is reached, prefatory reactions begin and dominate over sequent reactions, causing the cyclization of nitrile groups. Dehydrogentation reactions likely begin at approximately the same time as the cyclization reactions. In these early stages, no barrier to oxygen diffusion exists and oxygen is free to diffuse into the fiber. It is believed that the role of oxygen while the prefatory reactions dominate is to promote the cyclization of nitrile groups. The reaction rate of this stage of stabilization is limited by the formation of ladder polymer.

After a sufficient amount of the nitrile groups have undergone cyclization, the process of stabilization changes and sequent reactions dominate over prefatory reactions. During sequent reactions, it is believed that the ladder polymer formed during the prefatory reaction stage begins to cross-link. The oxygen that previously diffused into the fiber and accelerated the cyclization reactions promotes this cross-linking. The cross-linked ladder polymer forms a barrier to the further diffusion of oxygen into the sample

and the skin/core morphology is formed. The cross-linking of ladder polymer is also believed to be the source of the emerging peak noted at 25° 2θ, although this cannot be proven.

Treatment in oxygen environment at 1 atmosphere and treatment at higher pressures in air environment led to a one-zone morphology across the fiber cross-section. It is believed that because of the extra oxygen available for diffusion in the treatment environment, more oxygen was able to diffuse into the fiber during the prefatory reaction stage, before a barrier to diffusion was able to form. When the sequent reactions begin to dominate and cross-linking occurs, the morphology of the cross-section is already essentially uniformly oxidized.

5.4 Progression of Oxidation

Oxygen uptake during thermo-oxidative stabilization of PAN precursor is believed to be diffusion controlled. The diffusion of oxygen is difficult to quantify, however, due to the complex stabilization reactions taking place and the formation of a skin/core morphology after an unknown amount of stabilization occurs. The formation of a skin/core morphology is itself a mystery, but it has been found to be dependent on such factors as treatment temperature, fiber size, and fiber chemistry [28].

A skin/core morphology is noted in samples undergoing diffusion-limited reactions [28, 43]. The diffusion of oxygen into the samples is the rate-limiting step under these conditions, and the fiber properties generally change linearly with the square

root of time. However, the thermo-oxidative stabilization of PAN precursor cannot be simplified to either diffusion-limited or reaction-limited kinetics in many instances. As noted previously, when a skin/core morphology is first observed, the thickness of the skin layer already accounts for 40 to 50% of the fiber radius. It is believed that the oxidation of PAN is not solely responsible for the formation of the skin layer, and furthermore, the diffusion coefficient of oxygen in the core region is different from that in the skin region.

For purposes of discussion, a simplistic model for the diffusion of oxygen into PAN will be used. This model is based on the solution from Crank [58] for the diffusion of a gas into a solid cylinder consisting of a uniform phase. The solution to this problem is shown in Equation 3:

$$\frac{C - C_1}{C_0 - C_1} = 1 - \frac{2}{a}\sum_{n=1}^{\infty} \frac{e^{-D\alpha_n^2 t} J_0(r\alpha_n)}{\alpha_n J_1(a\alpha_n)} \qquad (3)$$

For this solution to be valid, it is necessary to consider a gas diffusing into a solid cylinder consisting of a uniform phase, as mentioned previously, as well as assuming that the surface concentration remains constant. In this equation, D is the diffusion coefficient, t is the time of diffusion, a is the fiber radius, r is the radial position measured from the center of the fiber, C is the concentration at r, C_0 is the surface concentration, C_1 is the initial concentration in the fiber, $J_0(x)$ is the Bessel function of the first kind of order zero, $J_1(x)$ is the Bessel function of the first order, and α is a root of Equation 4:

$$J_0(a\alpha_n) = 0 \qquad (4)$$

Solutions for Equation 3 can be written in terms of two dimensionless parameters, Dt/a^2 and r/a. Solutions of this type can be seen plotted in Figure 78.

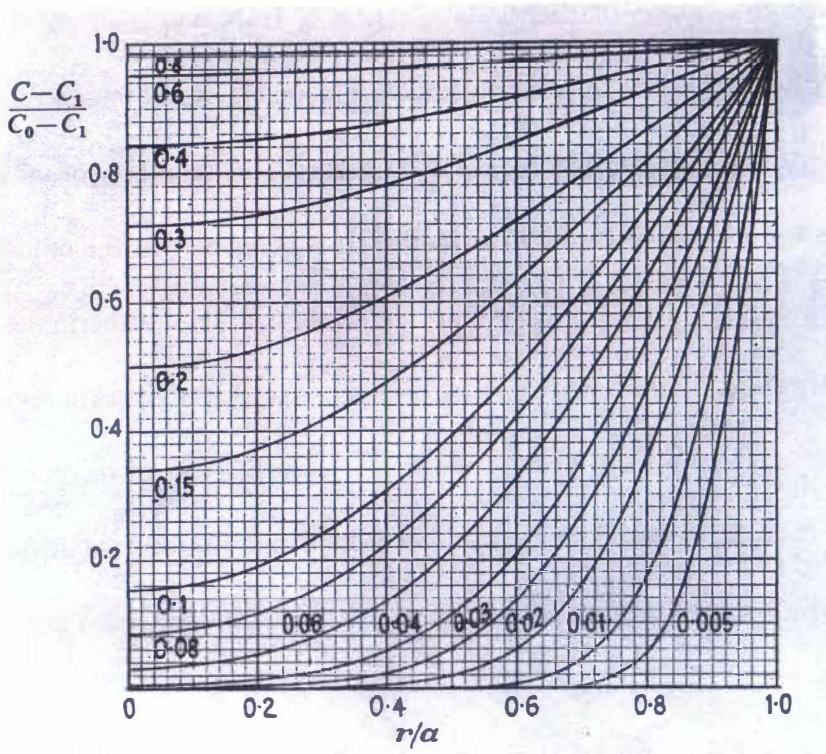

Figure 78. Concentration Distributions at Various Times.

C_1 is initial concentration and C_0 is surface concentration. Numbers on the curves are values of Dt/a^2 [59].

It is assumed that the surface concentration is controlled by the solubility of the gas in the cylinder and remains constant. The relationship between solubility coefficient, surface concentration, and pressure in polymeric materials is often given by Equation 5:

$$S = \frac{C_s}{P} \tag{5}$$

In this equation, S is the solubility coefficient, C_s is the surface concentration of the diffusing gas, and P is the partial pressure of the diffusing gas. Using both the solubility and the solutions to Equation 3 presented in Figure 78, the case of oxygen diffusion into PAN fiber can be considered.

The case of thermo-oxidative stabilization in air environment at atmospheric pressure will be considered. It is first necessary to obtain a value for C_0. It has been shown [28] that some fiber properties vary as the square root of time once the skin layer forms. Density data for samples treated at a soak temperature of 250°C in air at 1 atm was plotted in this manner and the density for the sample treated for 16 hours soak time, which showed a fully oxidized morphology upon acid treatment, was estimated to be approximately 1.6 g/cc. By assuming that the density increase in the sample is due solely to the uptake of oxygen, the oxygen concentration of the sample can be determined. A concentration of oxygen of approximately 27 wt% was found for this sample. This value was assumed to be an upper limit for the surface concentration, C_0, of oxygen during heat treatment. It is noted that if the actually value of surface concentration is lower, then the amount of diffusion that takes place will be reduced, not increased.

In order to follow the growth of the skin layer, it is necessary to know the minimum concentration of oxygen, C, necessary to prevent erosion upon acid treatment.

Jain and Abhiraman [26] state that a concentration of 8 to 12 wt% oxygen is necessary for full stabilization, and this concentration range is assumed to be that necessary to prevent attack upon treatment in sulfuric acid. The final concentration necessary is the initial concentration of oxygen present in the PAN fibers, C_l. This concentration is assumed to be 0% since it is not believed that a substantial amount of oxygen is trapped in the PAN as it is spun into fibers.

Information on diffusion coefficients of oxygen in PAN fiber is scarce. In order to calculate the diffusion coefficient at any given temperature, it is necessary to have both the pre-exponential factor and the activation energy for diffusion, neither of which is currently available for oxygen diffusing into PAN fiber. Warner et al. [28], however, estimated the diffusion coefficient of oxygen through the oxidized skin layer to be approximately 2×10^{-12} cm^2 sec^{-1} at 220°C.

For purposes of estimation, it is assumed that some amount of oxidation of PAN leading to the formation of a skin/core morphology took place during the ramp-up time of treatment. With this in mind, it is assumed that the oxidation of PAN begins at 180°C since it is believed that the stabilization reactions start at approximately this temperature. Also, it has been shown that treatment at lower temperatures does not cause significant changes from the precursor material. It is further assumed that the diffusion coefficient during the ramp-up time is approximately equal to that at 220°C. It is noted that this assumption results in an over-estimate in the diffusion taking place, since the diffusion coefficient at temperatures below 220°C should be lower than that at 220°C.

Using Figure 78 and the above assumptions, it is found that the skin layer after essentially 100 minutes at 220°C is estimated to be between 1.3 and 1.8 μm thick. However, it was found experimentally that after 60 minutes soak time, the skin thickness is 3.8 μm. The actual skin thickness observed experimentally is thicker than that estimated using the above assumptions. Thus, diffusion of oxygen is much more rapid in the fiber than is accounted for by this estimate. This implies that the skin layer does not form immediately and that the diffusion coefficient of oxygen in PAN is much higher before the skin/core morphology forms.

Using the above assumptions, it is also possible to estimate the apparent diffusion coefficient. It should be noted that this apparent diffusion coefficient is an average of the diffusion coefficient in the skin as well as the core material. For a sample treated at a soak temperature of 220°C for 60 minutes soak time, the apparent diffusion coefficient was found to range between 6.7×10^{-12} to 3.0×10^{-11} $cm^2\ sec^{-1}$. This range of values was estimated by varying the time for diffusion, t, the surface concentration, C_o, and the concentration at radial position r, C. The values chosen covered the range of values considered to be feasible. For example, reducing the diffusion time to 60 minutes at 220°C increases the diffusion coefficient relative to the initial choice of 100 minutes. Lowering C_o also increases the diffusion coefficient.

Similarly, for a sample treated at a soak temperature of 250°C for 6 hours soak time, the apparent diffusion coefficient of oxygen was estimated to range between 2.0 to 4.7×10^{-12} $cm^2\ sec^{-1}$. This range of values is thought to be more representative of the diffusion coefficient of oxygen in the skin layer, since a skin/core morphology is present

for the large part of treatment. This range of values is also found to be close to the diffusion coefficient of oxygen through the skin layer at 220°C estimated by Warner et al. [28].

The decrease in apparent diffusion coefficient as temperature is increased is counter-intuitive. The diffusion coefficient generally increases exponentially as the temperature is increased, as shown by Equation 6:

$$D = D_0 e^{-\frac{Q}{RT}} \tag{6}$$

In Equation 6, D is the diffusion coefficient, D_0 is the pre-exponential factor, Q is the activation energy for diffusion, R is the gas constant, and T is the temperature. It should be remembered, however, that the apparent diffusion coefficients being estimated are averages of diffusion coefficients in both the core material and the skin material. For the sample treated at 250°C for 6 hours, the diffusion coefficient of oxygen through the skin material accounts for a more significant portion of the average than it does for the sample treated at 220°C for 60 minutes. Since diffusion of oxygen through the skin material is reported to be slower than through the core material, the decrease in apparent diffusion coefficient as temperature and time are increased is reasonable.

Concordant with the progression of thermo-oxidative stabilization discussed previously, it is believed that in the beginning stages when prefatory reactions dominate, oxygen diffuses rapidly into the fiber. The diffusion coefficient of oxygen during this stage of stabilization is high, allowing for a majority of the fiber to be partially oxidized prior to the formation of a skin/core morphology.

In the later stages of stabilization, sequent reactions dominate and a skin/core morphology develops. In the core region of the fiber, the diffusion coefficient of oxygen would remain relatively high, yet in the skin region, the diffusion coefficient is much lower due to the cross-linked network of ladder polymer.

The formation of the skin/core morphology is thought to be related to the solubility of oxygen in the PAN fiber, especially for treatment in pure oxygen at 1 atmosphere and air at increased pressure. The equation governing solubility can be seen in Equation 3. For treatment in pure oxygen, the partial pressure of oxygen is essentially 5 times greater than treatment in air at atmospheric pressure. This increased partial pressure leads to a higher solubility and more oxygen diffuses into the fiber in the early stages of stabilization before the skin layer forms. Increasing the pressure of air during treatment also increases the partial pressure of oxygen, which in turn increases the solubility, leading to a similar effect. As noted previously, samples treated in pure oxygen had a uniform, fully oxidized fiber cross-section, as did samples treated in air at 5 atmospheres pressure. It is noted that both of these samples have essentially the same partial pressure of oxygen, and thus the same solubility.

In summary, based on the estimates given above, the apparent diffusion coefficient for a sample treated at a temperature of 220°C for 60 minutes soak time appears to be in the range of 6.7×10^{-12} to 3.0×10^{-11} cm^2 sec^{-1}. For a sample treated at 250°C for 6 hours, the apparent diffusion coefficient of oxygen appears to be in the range of 2.0 to 4.7×10^{-12} cm^2 sec^{-1}. It is noted that this latter range of diffusion coefficients is similar to the diffusion coefficient of oxygen through the skin layer proposed by Warner

et al. [28]. The decrease in the apparent diffusion coefficient as time and temperature are increased is believed to be due to the larger contribution that the diffusion coefficient of oxygen in the skin material has on the sample treated at 250°C and 6 hours. The model used for the estimates made is simplistic and does not take into account factors such as the moving diffusion boundary that is observed once the skin layer forms or the chemical reactions taking place during the thermo-oxidative stabilization process. It may be possible to make better estimates of the diffusion coefficients in the skin layer and the core material by taking these factors into consideration. It is also noted that solubility of oxygen in the PAN fiber appears to play an important role in the thermo-oxidative stabilization process.

5.5 Quantifying the Stabilized State of Polyacrylonitrile

With the results of this work's stabilization experiments presented, an important question arises: How is the fully stabilized state of polyacrylonitrile quantified? The present work presents three possibilities: (1) the morphological structure as measured by x-ray analysis is essentially amorphous, (2) the remnant heat as measured by DSC is approximately zero, and (3) the morphology of the fiber cross-section as determined by treatment in heated sulfuric acid is uniform and fully oxidized. The literature suggests two additional methods that could be used: (4) heat treat the fibers to an arbitrary temperature as determined by scanning a temperature range in the DSC, and (5) heat treat

the fibers to obtain the desired mechanical properties in the resultant carbon fiber upon subsequent carbonization.

Determining the amount of crystallinity remaining in the fiber sample is a relatively simple and quick analysis. As discussed previously, with sufficient soak time and soak temperature, the morphology of the PAN precursor is converted into an essentially amorphous structure, as measured by x-ray scattering. However, this essentially amorphous structure was noted in samples heat treated in nitrogen, air, and oxygen environments, but only treatment in air and oxygen environments yielded an emerging peak in the region of 25° 2θ. Treatment in nitrogen environment showed essentially no constructive interference in the region of 25° 2θ once the sample was converted into an essentially amorphous structure. This implies that there is a major structural difference between samples treated in nitrogen and those treated in oxygen-containing environments, but at the present time it is not clear just what this difference is.

The remnant heat of previously heat-treated fibers is also a relatively simply and quick analysis. Care must be taken when determining the remnant heat, however, because of the sparse literature concerning exact details of the measurements. In addition, values of remnant heat close to zero are not necessarily needed in order to obtain fibers that have been fully stabilized. Ubrìaco et al. [42] performed DSC analysis on pre-oxidized fibers supplied by Enichem Fibre. The fibers were heat treated at approximately 250°C in an oxidizing environment for about 3 hours. The amount of heat measured at a heating rate of 20°C/min in air purge gas was 262.5 J/g. The "Fully Stabilized" commercial sample studied in this work had a similar value of remnant heat,

281.38 ± 20 J/g. From these results, it is reasonable to conclude that a remnant heat of approximately 0 J/g is not necessary for "full stabilization".

Examining the fiber cross-section by etching the fiber samples in heated sulfuric acid is a much more involved process than determining crystallinity or measuring remnant heat. Also, it is very unlikely that the fibers must be fully oxidized in order to obtain full stabilization. The commercial "Fully Stabilized" sample was not fully chemically oxidized, as previously discussed. In order to obtain a fully oxidized fiber upon heat treatment, soak times of approximately 16 hours at 250°C in air environment are needed, or treatment in pure oxygen environment is required, as determined by this work. Both methods for obtaining a fully oxidized fiber are likely not feasible in commercial practice.

Using a small amount of precursor material for DSC analysis to obtain an arbitrary temperature at which to cease heat treatment is a quick and easy method for determining a maximum heat treatment temperature, but there is some dispute as to the validity of this technique in the literature. Fitzer et al. [35] state that for a PAN precursor containing 6% methyl acrylate and 1% itaconic acid, DSC measurements reveal that treatment should be stopped at 270°C to avoid over-oxidation of the fiber. Mather et al. [37] disagree, however. By studying a precursor supplied by Courtelle, which has approximately 6% methyl methacrylate, the authors state that a minimum temperature of 350°C and a maximum of 400°C seems to be essential for proper stabilization of PAN. One of their leading arguments is that at the higher temperatures, more hydrogen is removed from the sample, which should minimize tar formation during carbonization.

Improvements of 28% in the tensile strength and 9% in the tensile modulus were also noted in the carbon fibers formed upon subsequent carbonization.

In conclusion, the fifth and last method for quantifying the stabilized state of PAN seems to be the best: heat treat the fibers to obtain the desired mechanical properties in the resultant carbon fibers upon subsequent carbonization. This is obviously the most time consuming and difficult method since it requires the preparation of several samples to study the various variables in the carbon fiber production process. These variables include, but are not limited to: precursor composition, fiber tension during stabilization, stabilization heating rate, maximum stabilization treatment temperature, stabilization treatment time, and carbonization treatment temperature and time. Despite the large drawback, this method seems to be the most reliable due to the large number of variables in the stabilization and carbonization of polyacrylonitrile.

Chapter 6

Summary and Conclusions

In the stabilization of polyacrylonitrile precursor for the production of carbon fibers, temperature and time play important roles. Increases in soak temperature and soak time lower the crystallinity, increase the bulk density, and lower the remnant heat of the treated samples. By raising the soak temperature and shortening the soak time, it is possible to generate samples similar to those treated at lower soak temperature and higher soak time, within the limits of the analyses conducted in this work. This behavior was observed regardless of the treatment environment and treatment pressure.

Concerning the treatment environment, the presence of oxygen was found to promote the formation of an amorphous structure, higher density, and lower remnant heat values at lower soak temperature and soak times than would be necessary in inert environments. The presence of oxygen in the treatment environment also promotes the formation of the peak at 25° 2θ as compared to nitrogen environment.

For the oxidizing environments under consideration, the presence of excess oxygen in the treatment environment promoted an amorphous structure, higher density, and lower remnant heat values in a manner similar to that of an air environment for shorter soak times for a given soak temperature. For longer soak times, treatment in oxygen environment yielded fibers with higher densities and lower remnant heat values than those treated in air environment.

The effects of changes in treatment pressure were studied for both air and oxygen environments. Increasing the treatment pressure has little effect on the rate at which

density is increased or remnant heat is decreased at 0 minutes soak time. In addition, x-ray patterns taken from samples treated at varying pressures showed essentially no difference. For soak times of 60 minutes, the rates of density and remnant heat changes increases as the treatment pressure is increased. Once again, little difference is seen in the x-ray patterns as the treatment pressure is increased.

Based on the data presented, stabilization in an oxidizing environment seems to be preferable to stabilization in an inert environment. The presence of oxygen in the treatment environment promotes the formation of an amorphous structure and specifically the formation of an emerging peak at 25° 2θ, higher densities, and lower values of remnant heat at lower soak temperatures and lower soak times than would be required for treatment in an inert environment. On the other hand, though, it is debatable whether the presence of excess oxygen in the treatment environment improves stabilization, as previously discussed.

One possible advantage to carrying out stabilization in a pure oxygen environment is the formation of a uniform, fully oxidized structure across the fiber cross-section. The reasons behind the formation of a uniform, fully oxidized structure when fibers are treated in oxygen environment are not known, though it was suggested to be due to more rapid diffusion of oxygen into the sample before a cross-linked ladder structure sets up a barrier to diffusion. Treatment in air environment at atmospheric pressure leads to the formation of a skin/core morphology across the fiber cross-section, and it was found that it takes approximately 16 hours at 250°C to produce a fully oxidized fiber in air environment. Again, the importance of a uniform fiber cross-section is

debatable. It has been shown that commercially-treated "Fully Stabilized" fiber is not fully chemically oxidized.

A possible progression for the stabilization of PAN was presented. Essentially, during the first stage of stabilization, prefatory reactions dominate over sequent reactions. During this stage, oxygen is free to diffuse into the fiber, promoting the cyclization of nitrile groups. During the second stage of stabilization, sequent reactions dominate over prefatory reactions. Oxygen that previously diffused into the sample promotes the cross-linking of ladder polymer, leading to the formation of a skin/core morphology across the cross-section and a barrier to the further diffusion of oxygen.

A possible progression for the oxidation of PAN was also presented. By using a simplistic model and making certain assumptions, it was possible to estimate apparent diffusion coefficients at two temperatures. The apparent diffusion coefficient for a sample treated at 220°C for 60 minutes was estimated to be in the range of 6.7×10^{-12} to 3.0×10^{-11} cm^2 sec^{-1}. The apparent diffusion coefficient for a sample treated at 250°C for 6 hours was estimated to be in the range of 2.0 to 4.7×10^{-12} cm^2 sec^{-1}. It was also noted that the solubility of oxygen appears to play an important role in the diffusion, with samples treated in pure oxygen environment at one atmosphere and samples treated in air at 5 atmospheres both having fully oxidized fiber cross-sections.

Despite the various analyses performed on the heat-treated samples, it was impossible to quantify the fully stabilized state that is necessary for subsequent carbonization. It was decided that the best method for quantifying the fully stabilized

state was to simply study and characterize all of the possible variables by carrying out several stabilization and carbonization experiments.

Chapter 7

Future Work

In order to gain more information about the stabilization of PAN precursor, it is believed that performing FTIR analyses on heat treated samples will provide information on the changes in chemical structure brought about by stabilization. This will also help to clarify the differences that changes in temperature, time, environment, and pressure have on the stabilization of PAN.

It is recommended that PAN precursor with a larger fiber diameter is stabilized in a manner that will produce a two-zone morphology. Once this is performed, electron probe micro-analysis will provide information on the oxygen profile across the fiber cross-section as a result of stabilization. It will be necessary to determine a mounting procedure for the fibers that will not interfere with the electron probe micro-analysis.

Performing mechanical testing to determine the mechanical properties of the stabilized PAN would also help in determining the effects of temperature, time, environment, and pressure during stabilization.

After stabilization, carbonization of the stabilized fibers would prove to be informative. Mechanical testing of the resulting carbon fibers will help to further characterize the effects that temperature, time, environment, and pressure play during stabilization.

Finally, an attempt to mathematically model the stabilization and oxidation processes would be useful in assessing whether some of the ideas suggested above are reasonable.

References

References

1. J.-B. Donnet, T.K. Wang, J.C.M. Peng, and S. Rebouillat, eds. *Carbon Fibers: Third Edition, Revised and Expanded*. New York: Marcel Dekker, 1998.
2. M.S. Dresselhaus, G. Dresslhaus, K. Sugihara, I.L. Spain, and H.A. Goldberg. *Graphite Fibers and Filaments*. New York: Springer-Verlag, 1988.
3. J.I. Kroschwitz, ed. *Polymers: High Performance Polymers and Composites*. New York: John Wiley & Sons, 1991.
4. ®*PANOX - the oxidized fiber for textile applications* <http://www.sglcarbon.com/sgl_t/fibers/panox.html>.
5. "PYRON® Products." <http://www.zoltek.com/pyron_products/>.
6. W.D. Callister, Jr. *Materials Science and Engineering: An Introduction, Fifth Edition*. New York: John Wiley and Sons, 2000.
7. P.K. Mallick, H.S. Kliger, B.A. Wilson, C. Smith, and J. Stone. *Composite Materials Technology: Processes and Properties*. New York: Hanser Publishers, 1990.
8. E. Fitzer. "PAN-based carbon fibers - present state and trend of the technology from the viewpoint of possibilities and limits to influence and to control the fiber properties by the process parameters." *Carbon*. 27 (1989): 621-645.
9. "Medical materials." *Advanced Materials and Processes*. 160, No. 9 (2002): 24-27.
10. "Medical materials." *Advanced Materials and Processes*. 161, No.9 (2003): 26-30.
11. "Materials in sporting goods." *Advanced Materials and Processes*. 160, No. 9 (2002): 30-32.

12. "Advances in automotive materials." *Advanced Materials and Processes.* 161, No. 7 (2003): 18-22.

13. "Carbon fiber composite to replace glass in Corvette." *Advanced Materials and Processes.* 161, No. 8 (2003): 20.

14. "Advances in automotive materials." *Advanced Materials and Processes.* 161, No. 10 (2003): 37-42.

15. L.L. Vasiliev, L.E. Kanonchik, D.A. Mishkinis, and M.I. Rabetsky. "Adsorbed natural gas storage and transportation vessels." *International Journal of Thermal Science.* 39 (2000): 1047-1055.

16. N. Takeichi, H. Senoh, T. Yokota, H. Tsuruta, K. Hamada, H.T. Takeshita, H. Tanaka, T. Kiyobayashi, T. Takano, and N. Kuriyama. "Hybrid hydrogen storage vessel, a novel high-pressure hydrogen storage vessel combined with hydrogen storage material." *International Journal of Hydrogen Energy.*

17. K. Hanada, H. Shiono, and K. Matsuzaki. "Hydrogen uptake of carbon nanofiber under moderate temperature and low pressure." *Diamond and Related Materials.*

18. X. Zhang, and Z. Shen. "Carbon fiber paper for fuel cell electrode." *Fuel.* 81 (2002): 2199-2201.

19. H. Zhu, C. Li, X. Li, C. Xu, Z. Mao, J. Liang, and D. Wu. "Hydrogen storage by platelet-carbon fibers at room temperature." *Materials Letters.* 57 (2002): 32-35.

20. G.G. Tibbetts, P. Meisner, and C.H. Olk. "Hydrogen storage capacity of carbon nanotubes, filaments, and vapor-grown fibers." *Carbon.* 39 (2001): 2291-2301.

21. S.B. Warner, D.R. Uhlmann, and L.H. Peebles Jr. "Oxidative stabilization of acrylic fibres: Part 3 - Morphology of polyacrylonitrile." *Journal of Materials Science.* 14 (1979): 1893-1900.

22. M.K. Jain and A.S. Abhiraman. "Oxidative stabilization of oriented acrylic fibres - morphological rearrangements." *Journal of Materials Science.* 18 (1983): 179-188.

23. S. Dalton, F. Heatley, and P.M. Budd. "Thermal stabilization of polyacrylonitrile fibres." *Polymer.* (1999): 5531-5543.

24. M.K. Jain, M. Balasubramanian, P. Desai, and A.S. Abhiraman. "Conversion of acrylonitrile-based precursors to carbon fibres: Part 2 - Precursor morphology and thermooxidative stabilization." *Journal of Materials Science.* 22 (1987): 301-312.

25. W. Pinghua, L. Jie, Y. Zhongren, and L. Rengyuan. "Thermal oxidative stabilization of polyacrylonitrile precursor fiber - progression of morphological structure and mechanical properties." *Carbon.* 30 (1992): 113-120.

26. M.K. Jain and A.S. Abhiraman. "Conversion of arylonitrile-based precuror fibres to carbon fibres: Part 1 - A review of the physical and morphological aspects." *Journal of Materials Science.* 22 (1987): 278-300.

27. P. Bajaj, T.V. Sreekumar, and K. Sen. "Thermal behaviour of acrylonitrile copolymers having methacrylic and itaconic acid comonomers." *Polymer.* 42 (2001): 1707-1718.

28. S.B. Warner, L.H. Peebles Jr., and D.R. Uhlmann. "Oxidative stabilization of acrylic fibres: Part 1 - Oxygen uptake and general model." *Journal of Materials Science.* 14 (1979): 556-564.

29. E. Fitzer and D.J. Müller. "The influence of oxygen on the chemical reactions during stabilization of PAN as carbon fiber precursor." *Carbon.* 13 (1975): 63-69.

30. R.B. Mathur, O.P. Bahl, and J. Mittal. "Advances in the development of high-performance carbon fibres from PAN precursor." *Composites Science and Technology.* 51 (1994): 223-230.

31. L. Mascia and E.G. Paxton. "Physical changes during thermal oxidation of PAN fibres and effects of ?-radiation pre-treatment." *Thermochimica Acta.* 184 (1991): 251-267.

32. V.A. Bhanu, P. Rangarajan, K. Wiles, M. Bortner, M. Sankarpandian, D. Godshall, T.E. Glass, A.K. Banthia, J. Yang, G. Wilkes, D. Baird, and J.E. McGrath. "Synthesis and characterization of acrylonitrile methyl acrylate statistical copolymers as melt processable carbon fiber precursors." *Polymer.* 43 (2002): 4841-4850.

33. Z. Wangxi, L. Jie, and W. Gang. "Evolution of structure and properties of PAN precursors during their conversioin to carbon fibers." *Carbon.* 41 (2003): 2805-2812.

34. G.S. Bhat, F.L. Cook, A.S. Abhiraman, and L.H. Peebles Jr. "New aspects in the stabilization of acrylic fibers for carbon fibers." *Carbon.* 28 (1990): 377-385.

35. E. Fitzer, W. Frohs, and M. Heine. "Optimization of stabilization and carbonization treatment of PAN fibres and structural characterization of the resulting carbon fibers." *Carbon.* 24 (1986): 387-395.

36. A. Gupta and I.R. Harrison. "New aspects in the oxidative stabilization of PAN-based carbon fibers." *Carbon.* 34 (1996): 1427-1445.

37. R.B. Mathur, O.P. Bahl, and J. Mittal. "A new approach to thermal stabilisation of PAN fibres." *Carbon.* 30 (1992): 657-663.

38. N.V. Platonova, I.B. Klimenko, V.I. Grachev, and L.V. Smirnov. "Spectroscopic investigation of the thermooxidative degradation of polyacrylonitrile." *Polymer Science U.S.S.R.* 22 (1980): 2700-2710.

39. Z. Bashir. "A critical review of the stabiisation of polyacrylonitrile." *Carbon.* 29 (1991): 1081-1090.

40. H. Ogawa and K. Saito. "Oxidation behavior of polyacrylonitrile fibers evaluated by new stabilization index." *Carbon.* 33 (1995): 783-788.

41. C.L. Renschler, A.P. Sylwester, and L.V. Salgado. "Carbon films from polyacrylonitrile." *Journal of Materials Research.* 4 (1989): 452-457.

42. P. Ubbriaco, M. Petrella, and F. Tasselli. "Characterization of fibres from acrylic polymers for cement composites: DSC study." *Thermochimica Acta.* 227 (1993): 135-144.

43. G. Love, M.G.C. Cox, and V.D. Scott. "Electron-probe microanalysis of oxygen in heat-treated Orlon fibres." *Materials Research Bulletin.* 10 (1975): 815-818.

44. C. Blanco, S. Lu, S.P. Appleyard, and B. Rand. "The stabilisation of carbon fibres studied by micro-thermal analysis." *Carbon.* 41 (2003): 165-171.

45. W.J. Burlant and J.L. Parsons. "Pyrolysis of Polyacrylonitrile." *Journal of Polymer Science.* 22 (1956): 249-256.

46. S.C. Martin, J.J. Liggat, and C.E. Snape. "In situ NMR investigation into the thermal degradation and stabilisation of PAN." *Polymer Degradation and Stability.* 74 (2001): 407-412.

47. Y.P. Romanova, I.G. Rumynskaya, M.L. Syrkina, and Y.I. Firsov. "Aspects of the formation of polyconjugated structures during thermal and oxidative degradation of polyacrylonitrile." *Polymer Science U.S.S.R.* 28 (1986): 50-59.

48. S.B. Warner, L.H. Peebles Jr., and D.R. Uhlmann. "Oxidative stabilization of acrylic fibres: Part 2 - Stabilization dynamics." *Journal of Materials Science.* 14 (1979): 565-572.

49. L. Laffont, M. Monthioux, V. Serin, R.B. Mathur, C. Guimon, and M.F. Guimon. "An EELS study of the sturctureal and chemical transformation of PAN polymer to solid carbon." *Carbon.* 42 (2004): 2485-2494.

50. A. Gupta and I.R. Harrison. "New aspects in the oxidative stabilization of PAN-based carbon fibers: II." *Carbon.* 35 (1997): 809-818.

51. A. Takaku, T. Kobayashi, S. Terui, N. Okui, and J. Shimizu. "Changes of tensile modulus and contractive stress of acrylic fibres during thermal stabilisation for carbon fibre production." *Fibre Science and Technology.* 15 (1981): 87-98.

52. O.P. Bahl and R.B. Mathur. "Effect of load on the mechanical properties of carbon fibres from PAN precursor." *Fibre Science and Technology.* 12 (1979): 31-39.

53. M.G. Dunham and D.D. Edie. "Model of stabilization for PAN-based carbon fiber precursor bundles." *Carbon.* 30 (1992): 435-450.

54. M. Minagawa and T. Iwamatsu. "Relation between the thermal behavior of polyacrylonitrile and polymerization factors." *Journal of Polymer Science: Polymer Chemistry Edition.* 18 (1980): 481-494.

55. L.H. Peebles, Jr, P. Peyser, A.W. Snow, and W.C. Peters. "On the exotherm of polyacrylonitrile: pyrolysis of the homopolymer under inert conditions." *Carbon.* 28 (1990): 707-715.

56. D.A. Grove III and A.S. Abhiraman. "A mathematical model of solid-state thermo-oxidative stabilization of acrylic fibers." *Carbon.* 30 (1992): 451-457.

57. L.M. Manocha and O.P. Bahl. "Role of oxygen during thermal stabilisation of PAN fibres." *Fibre Science and Technology.* 13 (1980): 199-212.

58. J. Crank. *The Mathematics of Diffusion.* New York: Oxford University Press, 1967.

Vita

Stephen Alan White was born in Morristown, TN on October 7, 1979. He was raised in Jefferson City, TN. He attended Jefferson Elementary and Jefferson Middle School. He graduated from Jefferson County High School in 1998. From there, he went to the University of Tennessee, Knoxville and received a B.S. in materials science and engineering in 2002.